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PROCEEDINGS.

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1928.

THE PHYSICAL SOCIETY

1928-29.

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INSTRUCTIONS TO AUTHORS.

NOTE.—The acceptance of a Paper for publication in the Proceedings rests with the Council, advised by its Editing Committee. The high cost of printing renders it imperative to exclude matter that is not novel or not of importance to the understanding of the Paper.

Authors offering original contributions for publication in the Proceedings should observe the following directions: failure to comply with these may cause considerable delay in publication. (Fuller directions, including special instructions on the arrangement of mathematical work, are contained in a special leaflet obtainable from the Secretaries.)

Manuscript.—In drafting the Paper a clear and concise style should be adopted. The utmost brevity should be used consistent with effective presentation of the original subject-matter.

The MS. should be easily legible (preferably typewritten and double-spaced). It should receive a careful final revision before communication, since alterations are costly once the type has been set up.

Mathematical expressions should be set out clearly, in the simplest possible notation.

Drawings and Tables.—Diagrams must be carefully drawn on white paper or card, in indian ink, of size and thickness of line sufficient to allow of reduction. Lettering and numbering should be in *pencil*, to allow of printing in a uniform style. The number of diagrams should be kept down to the minimum. Data should in general be presented in the form of either curves or tables, but not both.

Footlines descriptive of figures, and headlines indicative of contents of tables, should be supplied.

Abstracts.—MSS. must be accompanied by an abstract, brief but sufficient to indicate the scope of the Paper and to record all novel results.

Proofs.—Proofs of accepted Papers will be forwarded to Authors, and should be returned promptly with errors corrected, but additions to or other deviations from the MS. should be avoided.

Reprints.—Fifty copies of printed Papers will be supplied gratis. Extra copies may be purchased at cost price.

Contributions by Non-Fellows.—Papers by non-Fellows must be communicated to the Society through a Fellow.

Republication.—Permission to reproduce Papers or illustrations contained therein may be granted by the Council on application to the Hon. Secretaries.

GROUP PHOTOGRAPH TAKEN ON THE OCCASION OF THE VISIT OF THE PHYSICAL SOCIETY TO BRISTOL, JULY 7, 1928.

PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY.

SESSION 1927-1928.

Except where the contrary is stated, the Meetings were held at the Imperial College of Science, the President being in the Chair.

October 28, 1927.

E. H. RAYNER, M.A., Sc.D., in the Chair.

A DEMONSTRATION of an Improved Mercury Vapour Trap was given by Prof. G. I. FINCH, M.B.E.

The following Papers were read :—

"Theory of Liquid Flow Through Cones," by W. N. BOND, M.A., D.Sc., F.Inst.P.

"The Structure of Smoke Particles from a Cadmium Arc," by H. P. WALMSLEY, M.Sc.

November 11, 1927.

The following were elected Fellows of the Society: R. P. G. Denman, M.A., A.M.I.E.E.; Rupert Woodville Hardisty; Prof. Arnold Crowther, M.A., Sc.D.; Prof. Harold John Taylor, B.Sc.; Raymond William Crabtree, B.Sc. The President announced that the Council had elected the following Student Members: Frederick G. Filby; Arthur Stanley Radford; Ernest Gordon Cox; Frank Gill; Cyril Alfred Sinfield; R. A. Fereday; John Bernard Charters; Morris Ernest Sions.

The following Papers were read :—

"The Power Factor and Capacity of the Electrodes and Base of Triode Valves, with Special Reference to their use in Thermionic Rectifiers," by G. W. SUTTON, B.Sc.

"The Refraction and Dispersion of Air, Oxygen and Gaseous Chloroform; and New Determinations of the Gaseous Refractivities of Acetone, Methyl Ether, and Ethyl Ether," by H. LOWERY, M.Sc.

"Theory of the Elastic Pianoforte Hammer," by PANCHANON DAS, M.Sc.

A DEMONSTRATION was given by Mr. C. O. BROWNE, of Messrs. Adam Hilger, Ltd., of an experiment due to Prof. Kerr Grant, in which a beam of light is made to fluctuate in intensity at radio frequencies in synchronism with the piezo-electric oscillations of a quartz crystal.

November 25, 1927.

E. H. RAYNER, M.A., Sc.D., in the Chair.

The following were elected Fellows of the Society: Geo. E. Harrison, M.Sc.; M. O. Pelton, B.Sc.

The following Papers were read:—

"On the Measurement of the Electrical Resistance of Porous Materials," by A. E. KNOWLER, M.Sc., A.Inst.P.

"Regularities in the Spectrum of Ionised Neon," by P. K. KICHLU, M.Sc.

"A Calorimeter for the Determination of the Heat Developed by Fruit," by EZER GRIFFITHS, D.Sc., F.R.S.

A series of Lantern Slides illustrating Air Conditioning Experiments, with especial reference to Fruit Storage, were shown by EZER GRIFFITHS, D.Sc., F.R.S.

December 9, 1927.

The following was elected a Fellow of the Society: Percy Wilson, M.A. The President announced that the Council had elected the following a Student Member of the Society: Robert William Sutton.

The following Papers were read:—

"The Scattering of Light by Individual Particles in Smokes," by H. P. WALMSLEY.

"On the Construction and Standardisation of an Interferometer Pressure Gauge," by J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford.

"The Dielectric Constant of Liquid Bromine," by ANNE I. ANDERSON, B.Sc.

January 10, 11 and 12, 1928.

The Eighteenth Annual Exhibition of Electrical, Optical and other Physical Apparatus was held by the Physical and Optical Societies at the Imperial College of Science.

January 27, 1928.

The following was elected a Fellow of the Society: Charles Edwin Foster. The President announced that the Council had elected the following a Student Member of the Society: Solomon Zeidenfeld.

The following Papers were read:—

"The Swan Band Spectrum of Carbon," by W. E. PRETTY, A.R.C.S., B.Sc.

"On Some Misapplications of the Law of Errors, and on the Intrinsic Error in Focometry," by T. SMITH, M.A., F.Inst.P.

"Some Acoustical Phenomena Illustrated by Ripples—Transmission through Quincke Filters, Curved Conduits and Vibrating Partitions," by A. H. DAVIS, D.Sc.

February 10, 1928.

The following were elected Fellows of the Society: Harold Ashley Daynes, Reginald Carr Brown, George Morris.

The following Papers were read:—

"A Simple Graphical Method for the Determination of Galvanometer and Fluxmeter Constants; with a Note on the Measurement of Intense Magnetic Fields," by ALLAN FERGUSON, D.Sc., and E. J. IRONS, B.Sc.

"On a Method of Constructing the Caustic Curve formed by Refraction at a Plane Surface," by C. J. SMITH, Ph.D.

"The Application of Electrical Resistance Measurements to the Study of Atmospheric Corrosion of Metals," by J. C. HUDSON.

February 24, 1928.

The following Papers were read:—

"Some Methods of Estimating the Intensities of Spectral Lines," by W. H. J. CHILDS, B.Sc., Demonstrator in Physics, King's College, London.

"Electrical Methods of Hygrometry," by P. W. BURBIDGE, M.Sc., B.A., Professor of Physics, and N. S. ALEXANDER, M.Sc., Auckland University College, New Zealand.

March 9, 1928.

The President announced that the Council had elected the following a Student Member of the Society: H. Harrison Macey.

The Thirteenth Guthrie Lecture was delivered by Prof. Sir J. J. THOMSON, O.M., F.R.S., who took as his subject "Electrodeless Discharges through Gases."

A vote of thanks to the lecturer was proposed by Sir OLIVER LODGE, D.Sc., F.R.S., seconded by ALEXANDER RUSSELL, M.A., D.Sc., F.R.S., and carried by acclamation.

March 23, 1928.

Annual General Meeting.

The Report of the Council and that of the Hon. Treasurer were presented and unanimously adopted.

REPORT OF THE COUNCIL.

During the year fourteen Ordinary Science Meetings have been held at the Imperial College of Science. At these meetings 39 Papers were presented and 13 Demonstrations were given. A Special Meeting was held on June 3, at which Dr. E. H. Rayner gave a lecture on "The Total Eclipse of the Sun." About 75 Fellows and Visitors were present. About 250 Fellows, Students and Friends of the Society went to Richmond (Yorkshire) for the purpose of seeing the Total Eclipse of the Sun on the morning of June 29. On the return journey some hours were spent in York.

Prof. Sir Ernest Rutherford, O.M., P.R.S., delivered the Twelfth Guthrie Lecture on February 25, the subject being "Atomic Nuclei and their Disintegration." About 160 Fellows and Visitors were present.

The average attendance at the meetings of the Society was 57.

The Seventeenth Annual Exhibition, arranged jointly by the Physical and Optical Societies, was held, through the courtesy of the Governing Body, at the Imperial College, on January 4, 5 and 6. Trade Exhibits were arranged by seventy-four firms, and the recently instituted Research and Experimental Section contained exhibits contributed from thirty-two sources. Discourses were given by Dr. C. V. Drysdale on "Progress in Electrical Instrument Design and Construction"; by Mr. J. L. Baird on "Television";

and by Prof. E. N. da C. Andrade, whose discourse consisted of a full-dress impersonation of Francis Hawksbee giving an experimental lecture in the time of Queen Anne. On the third day the general public was admitted. The total attendance at the Exhibition was estimated at over four thousand.

A Joint Committee of the Physical and Optical Societies has been formed to deal with all matters concerning the Annual Exhibition, with Mr. T. Martin (Secretary of the Institute of Physics) as Secretary.

Dr. D. Owen and Dr. J. H. Vincent have been reappointed as representatives of the Society on the Board of the Institute of Physics ; and Mr. J. Guild and Dr. D. Owen on the Science Abstracts Committee. Mr. T. Smith has been appointed as the Society's delegate to the Organising Committee of the Seventh International Congress of Photography ; Dr. A. Ferguson has been appointed as the Society's representative on the National Council for Physics ; and Dr. E. H. Rayner will represent the Society on the National Committee for Radio-telegraphy.

Prof. H. A. Wilson and Prof. W. F. G. Swann represented the Society at the Bicentenary Celebrations of the American Philosophical Society, held at the end of April, and presented a letter of congratulation from the Society. The President, Prof. O. W. Richardson, represented the Society and presented an address at the International Congress of Physicists, held in September at Como in honour of Alessandro Volta. Mr. F. Twyman represented the Society at the Fresnel Centenary Celebrations, held in Paris at the end of October, and conveyed an address to the Société Française de Physique. Prof. A. Fowler represented the Society at the opening of the new Physics Laboratories at Bristol in October.

The Council has awarded the Fifth Duddell Medal to Dr. F. E. Smith, F.R.S. This will be presented at the Annual General Meeting.

The Report on Series in Line Spectra, by Prof. A. Fowler, has been reprinted with an additional index.

A Special Sub-committee has been formed to consider all questions dealing with publications issued by the Society. In consequence of its preliminary reports, the Council has given notice of the termination of its printing and publishing agreement with the Fleetway Press, and has made arrangements with the Cambridge University Press for the printing of its publications in the future. A leaflet prepared by the Sub-committee, entitled "Instructions to Authors," has been issued, which, it is hoped, will effect at the same time an improvement in the accuracy and a reduction in the cost of printing Papers in the Proceedings. The recommendations contained in the leaflet have been adopted by the Optical Society, and are under consideration by other societies.

As a result of the negotiations with the Institute of Physics, which were referred to in the last Annual Report, it has been arranged that some of the routine business

of the Society shall be performed by the Institute. The registered address of the Society has been changed to 1, Lowther Gardens, South Kensington, S.W.7.

In view of the difficulty in getting the accounts audited as early as the second Friday in February, the Council has arranged to hold the Annual General Meeting on the fourth Friday in March. It is anticipated that a similar date will be selected in future years.

Prof. Sir Arthur Schuster, K.B.E., F.R.S. (Past-President, 1912-1914), has tendered his resignation as Foreign Secretary. The Council has accepted with regret his resignation of the duties which he has so ably fulfilled since 1920, and records the great indebtedness of the Physical Society to him for his valued service.

The Council records with regret the death of Prof. Svante Arrhenius, who was elected an Honorary Fellow of the Society in 1910.

It is necessary also to record with regret the deaths of Prof. W. H. Coleman (elected 1890), Prof. R. A. Lehfeldt (elected 1895), and Prof. A. Liversidge (elected 1876), all Life Fellows of the Society ; also of Mr. E. F. Etchells (elected 1904), Major J. R. Erskine-Murray (elected 1902), and Prof. A. W. Scott (elected 1883).

The number of Honorary Fellows on the Roll on December 31, 1927, was 11. At the same date Ordinary Fellows numbered 680 and Students 27.

The changes in the membership of the Society during the year are shown in the appended Table :—

——	Total Dec. 31, 1926.	Changes during 1927.		Total Dec. 31, 1927.
Honorary Fellows...	12	Deceased	1	
		Net decrease	1	11
Ordinary Fellows ...	666	Elected	26	
		Student transfers	0	
			26	
		Deceased ...	6	
		Resigned or lapsed	6	
			—12	
		Net increase	14	680
Students	12	Elected	16	
		Resigned	1	
		Net increase	15	27
Total Membership...	690	Net increase	28	718

REPORT OF THE HON. TREASURER.

The Income for the year 1927 exceeded the Expenditure by £29 14s. 8d. This is satisfactory when it is considered that the Society has had to reprint three Parts of the Proceedings of the Society which were out of print, and the report of Prof. Fowler on "Series in Line Spectra," which was also out of print. The Society is indebted to the Council of the Royal Society for the grant of £50 towards the cost of printing Prof. Fowler's report, and also for a further grant of £100 towards the cost of its publications. The valuation of the publications of the Society in the Balance Sheet has been increased from £400 (the figure at which it has stood for the last few years) to £500. It has been considered advisable to do this, as the addition of the Parts of the Proceedings which have been reprinted, and the recently instituted increase in the price of the Proceedings, have materially increased the value of the publications in stock.

It is gratifying to notice that by slightly stricter control of the length of Papers, and the number and size of the illustrations, a reduction of over £100 has been made in the cost of printing Volume 39 of the Proceedings as compared with Volume 38.

The Society has not received any remission of taxes on its investment income for 1926, and no amount has been included in the Balance Sheet for a refund in the 1927 accounts. This is due to the whole question of the remission of taxes to scientific societies being *sub judice*. It is hoped that on some future occasion it will be possible to report that the taxes have been refunded.

The sum of £112 10s. 0d. was paid to the Institute of Physics for secretarial and other work carried out on behalf of the Society by the Institute during the latter part of the year, and this sum includes the preparatory work for the 1928 Exhibition. The item "other expenses" under the heading of "Administration" includes the secretarial and accountancy expenses of the Society before the offices were transferred to 1, Lowther Gardens. It also includes some new furniture and expenditure connected with the transfer.

A legacy of £250, free of legacy duty, was received from the Executors of the late Prof. A. W. Scott, of St. David's College, Lampeter, in July, 1927, and was invested in 5 per cent. War Loan Stock.

At the request of the Treasurer, the Council appointed a Finance Committee to advise on the various financial questions that may arise.

The investments have been valued at market prices through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank.

INCOME AND EXPENDITURE ACCOUNT.

For the Year ended 31st December, 1927.

1926. £ s. d.	EXPENDITURE.	£ s. d.	£ s. d.
	To		
	Stock of Publications 1st January, 1927 ...		400 0 0
434 0 0	"Science Abstracts"		475 0 0
	Ordinary Publications :—		
1,053 6 1	"Proceedings"	922 0 8	
73 3 3	"Bulletin"	73 15 4	
92 17 10	General	101 17 3	
			1,097 13 3
	Reprints		188 12 7
115 9 4	Postage of Publications		105 0 10
61 12 3	Reporting		61 8 5
37 12 0	Refreshments and Expenses of Meetings...		33 15 2
369 12 7	Exhibition Expenses		485 15 10
8 8 4	Periodicals and Library		5 0 0
23 16 9	*Secretary and Treasurer's Expenses.*		
	Administration :		
	Payment to Institute of Physics as from April 1st, 1927	112 10 0	
15 9 5	Other Expenses	100 8 7	
			212 18 7
20 0 0	Guthrie Lecture (Honorarium)		20 0 0
21 0 0	Optical Society—Exhibition Account		10 4 5
	Expenses of Eclipse Excursion		384 15 0
	Expenses of Delegates to Volta Congress and Fresnel Centenary		26 13 6
10 6 0	*Participation in "Coming-of-Age" Celebrations, Sheffield University.*		
	A. W Scott Bequest: Purchase of £250 5% War Loan		255 11 7
	Balance being excess of Income over Expenditure carried to Accumulated Fund		29 14 8
£2,366 13 10			£3,792 3 10

1926. £ s. d.	INCOME.	£ s. d.	£ s. d.
	By		
	Stock of Publications, 31st December, 1927		500 0 0
	Subscriptions :		
1,063 3 11	Fellows*	1,113 17 1	
9 9 0	(Voluntary†)	9 9 0	
8 18 6	Students	8 5 0	
52 18 6	for "Science Abstracts" and Advance Proofs	64 5 0	
		1,195 16 1	
1,134 9 11	*Less* Subscriptions written off	4 4 0	
			1,191 12 1
	Sale of Publications (Fleetway Press, Ltd.)		630 16 2
	Dividends from Investments	191 8 6	
169 11 4	*Less :* Transferred to Duddell Memorial Trust Fund	20 0 0	
			171 8 6
12 16 11	Interest on Deposit Account		6 9 7
29 10 11	*Income Tax repayable.*		
434 8 0	Exhibitors' Payments on account of Exhibition Catalogue		507 2 6
100 0 0	Royal Society Grant for Publications...		150 0 0
	Eclipse Excursion : Receipts from Sale of Tickets		384 15 0
	A. W. Scott Bequest		250 0 0
1 6 1	*Balance being excess of Expenditure over Income.*		
£2,366 13 10			£3,792 3 10

* Sixty-four Fellows paid reduced subscriptions by the arrangement with the Institute of Physics, the total rebate amounting to £23 4s. 6d.

† "Voluntary Subscriptions" are subscriptions paid by Fellows who compounded for the low sum of £10.

BALANCE SHEET AT DECEMBER 31ST, 1927.

LIABILITIES.	£ s. d.	£ s. d.
Accumulated Fund :—		
Balance as per last account	1,878 17 11	
Entrance Fees, 1927	30 9 0	
	1,909 6 11	
Add Increased Value of Investments	57 0 0	
Excess of Income over Expenditure, 1927	29 14 8	
		1,996 1 7
Life Compositions :—		
As per last Balance Sheet		2,289 10 0
Duddell Memorial Trust Fund :—		
As per last Balance Sheet	429 12 9	
Add Increased Value of Investments	1 0 0	
		430 12 9
W. F. Stanley Trust Fund :—		
As per last Balance Sheet	428 0 0	
Less Decreased value of Investments	42 0 0	
		386 0 0
A. W. Scott Bequest		250 0 0
Sundry Creditors		304 18 9
Subscriptions paid in advance		19 8 6
		£5,676 11 7

ASSETS.	£ s. d.	£ s. d.
Investments at Market Value on date :—		
£399 London Midland & Scottish Railway 4 per cent. Debenture Stock	319 0 0	
£1,000 London Midland and Scottish Railway 4 per cent. Preference Stock	750 0 0	
£200 Metropolitan Board of Works 3½ per cent. Stock	194 0 0	
£400 Lancaster Corporation 3 per cent. Redeemable Stock	268 0 0	
£254 2s. 9d. New South Wales 5 per cent. Stock, 1935-55	248 0 0	
£300 Southern Railway Preferred Ordinary Stock	221 0 0	
£442 Southern Railway Deferred Ordinary Stock	165 0 0	
£500 London & North Eastern Railway 4 per cent. Debenture Stock	392 0 0	
£500 India 3½ per cent. Stock	360 0 0	
£650 4% Funding Loan, 1960/90	573 0 0	
£550 5% War Loan 1929/47 inscribed, "A" Account	556 0 0	
£400 5% War Loan 1929/47 inscribed, "B" Account (Duddell Memorial Fund)	404 0 0	
£150 Southern Railway 5 per cent. Debenture Stock	150 0 0	
		4,600 0 0
Stock of Publications (as per Treasurer's valuation)		500 0 0
Subscriptions due		57 15 0
Due from Fleetway Press		282 17 1
Due from Inland Revenue—Income Tax Reclaimed (as per last Balance Sheet)		27 10 10
Cash at Bank	203 13 3	
Cash in Hand	4 15 5	
		208 8 8
		£5,676 11 7

ROBERT S. WHIPPLE.—*Honorary Treasurer.*

We have audited the above Balance Sheet and have obtained all the information and explanations we have required. We have verified the Bank Balance and the Investments. In our opinion such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the Society's affairs according to the best of our information and the explanations given to us and as shown by the books of the Society.

Spencer House,
South Place, E.C.2.
March 5th, 1928.

KNOX, CROPPER & CO.,
Chartered Accountants.

Examined and approved on behalf of the Society { (Signed) G. H. Baillie. (Signed) L. Hartshorn.

LIFE COMPOSITION FUND AT DECEMBER 31ST, 1927.

		£	s.	d.
128	Fellows paid £10	1,280	0	0
3	Fellows paid £15	45	0	0
1	Fellow paid £20	20	0	0
1	Fellow paid £20 10s.	20	10	0
14	Fellows paid £21	294	0	0
20	Fellows paid £31 10s.	630	0	0
167		£2,289	10	0

W. F. STANLEY TRUST FUND (FOR THE "BULLETIN").

	£	s.	d.		£	s.	d.
£300 Southern Railway Preferred Ordinary Stock	221	0	0	Carried to Balance Sheet	386	0	0
£442 Southern Railway Deferred Ordinary Stock	165	0	0				
	£386	0	0		£386	0	0

DUDDELL MEMORIAL TRUST FUND.

CAPITAL

	£	s.	d.		£	s.	d.
£400 War Loan 5% 1929/47 inscribed Stock	404	0	0	Carried to Balance Sheet	404	0	0

REVENUE.

	£	s.	d.		£	s.	d.
Balance at 31st December, 1926	26	12	9	Honorarium to Medallist	20	0	0
Dividends	20	0	0	Balance carried to Balance Sheet	26	12	9
	£46	12	9		£46	12	9

Presentation of the Duddell Medal.

The Duddell Memorial Medal for 1928 was presented to F. E. Smith, C.B., C.B.E., D.Sc., F.R.S.

Prof. O. W. Richardson, President of the Society, in making the presentation, said that, after considering the terms of the Duddell Medal Foundation, the Council had unanimously chosen Dr. Smith as the medallist for this year, in view of the distinguished part he has played in promoting the accuracy of electrical measurements. He became head of the Electrical Standards Department of the National Physical Laboratory on its foundation in 1901, and soon achieved world-wide fame for his work on the British Association Standards of Resistance. His research at the N.P.L. included important developments in precision bridge methods and standard cells, an absolute current balance accurate within 2 parts in 100,000, devices for measuring resistance and the earth's magnetic field in C.G.S. units, a new magnetograph and a new silver voltameter, the latter having come into international use. During the war he devised a number of instruments for the use of the fighting services, and he was appointed first Director of Research at the Admiralty in 1919. He had contributed to the progress of science no less ably on the administrative than on the experimental side, not only as Hon. Secretary of the British Association and in similar offices of a general character, but, as Fellows would remember with gratitude, as Hon. Secretary (Business) for many years and ultimately President (1924/1925) of the Physical Society, whose flourishing condition was in no small measure due to his enthusiasm. In his Presidential Address in 1925 he had urged the international adoption of the C.G.S. electrical units and the gradual abolition of the present international standards, and it was pleasing to know that this proposal had been endorsed by the International Committee on Weights and Measures which met at Sèvres in 1927. He had advocated in season and out of season the intensive improvement of instrument design and construction in order that the advance of knowledge might not be retarded by the present limits of accurate measurement. He was also an enthusiastic advocate of a stronger emphasis on experimental accuracy in the teaching of science.

Dr. F. E. Smith expressed his gratitude for the award. He appreciated it particularly because of his friendship with Duddell and of his regard for the Physical Society, with which he had been so intimately associated. Duddell was not only a brilliant designer, but an exceptionally clever hand-worker, and he had been a source of inspiration to all who had the interests of experimental accuracy at heart. Dr. Smith added that he had first become interested in precision measurements when as a student of the Royal College of Science he had worked under Prof. Watson on absolute electromagnetic determinations, and in those days he had learned much from Sir A. Rücker and Prof. Boys, whose measurements of minute quantities he had always followed with great interest. The Physical Society had always attached due importance to experimental methods, and he had followed with satisfaction the growth of the Annual Exhibition of Apparatus, which had increased from a small beginning until it now attracted 200 exhibitors and 5,000 visitors. He believed that as it continued to grow it would play an important part in focussing interest on the development of instrument design, as regards both the devising of new instruments and the improvement of old models, with the view of obtaining increased accuracy.

Election of Council.

Dr. J. S. Anderson and Mr. J. H. Coste having been appointed scrutators, the Officers and Council for 1928-1929 were elected as follows :—

President.—W. H. Eccles, D.Sc., F.R.S.

Vice-presidents who have filled the office of President.—Sir Oliver J. Lodge, D.Sc., F.R.S., Sir Richard Glazebrook, K.C.B., D.Sc., F.R.S., C. Chree, Sc.D., LL.D., F.R.S., Prof. H. L. Callendar, M.A., LL.D., F.R.S., Sir Arthur Schuster, Ph.D., Sc.D., F.R.S., Sir J. J. Thomson, O.M., D.Sc., F.R.S., Prof. C. Vernon Boys, F.R.S., Prof. C. H. Lees, D.Sc., F.R.S., Prof. Sir W. H. Bragg, K.B.E., M.A., F.R.S., Alexander Russell, M.A., D.Sc., F.R.S., F. E. Smith, C.B., C.B.E., D.Sc., F.R.S., Prof. O. W. Richardson, M. A., D.Sc., F.R.S.

Vice-presidents.—R. W. Paul, Prof. E. A. Owen, M.A., D.Sc., D. Owen, B.A., D.Sc., Prof. F. L. Hopwood, D.Sc.

Hon. Secretaries.—Prof. A. O. Rankine, O.B.E., D.Sc., J. Guild, A.R.C.S., D.I.C.

Hon. Foreign Secretary.—Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

Hon. Treasurer.—R. S. Whipple.

Hon. Librarian.—J. H. Brinkworth, M.Sc., A.R.C.S.

Ordinary Members of Council.—Miss A. C. Davies, D.Sc., Prof. A. M. Tyndall, D.Sc., T. Smith, M.A., A. Ferguson, M.A., D.Sc., J. S. G. Thomas, D.Sc., Prof. E. V. Appleton, M.A., D.Sc., F.R.S., Sir Richard Paget, Bart., Prof. E. N. da C. Andrade, D.Sc., Ezer Griffiths, D.Sc., F.R.S., A. B. Wood, D.Sc.

Election of Honorary Fellow.

Prof. Albert Einstein was unanimously elected an Honorary Fellow of the Society.

Votes of Thanks.

A vote of thanks to the Hon. Auditors was proposed by Mr. Robert Whipple and seconded by Prof. F. L. Hopwood. A vote of thanks to the retiring Officers and Council was proposed by Dr. W. H. Eccles and seconded by Dr. J. H. Vincent. A vote of thanks to the Governors of the Imperial College was proposed by Mr. T. Smith and seconded by Dr. J. S. G. Thomas. The votes of thanks were carried by acclamation.

Ordinary Meeting following the Annual General Meeting.

The following were elected Fellows of the Society: John William Avery, A.R.C.S., D.Sc., D.I.C. (previously a Student Member), Martin W. Strong, B.Sc. The President announced that the Council had appointed the following to be Student Members: Hugh Charles Tett, Sidney T. Newing, John Rankine.

The following Papers were read :—

"The Terminal Velocity of Drops," by W. D. Flower, B.Sc.

"On the Longitudinal Waves along a Rod," by Satyandra Ray, M.Sc., Government College, Ajmer, India."

"On the Damping of Mercury Ripples,'" by J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford.

A DEMONSTRATION of *Die Rastermethode* (the testing of spherical aberration by means of shadows in an astigmatic beam) was given by J. E. CALTHROP, M.A., M.Sc.

April 27, 1928.

The following were elected Fellows of the Society: S. N. Banerji, M.Sc.; Maurice Milbourn, A.R.C.S., B.Sc., D.I.C.

The President announced that Mr. J. Guild had been obliged to resign the Honorary Secretaryship (Papers) of the Society for reasons of health. He expressed the deep regret felt by the Council, and moved a vote of thanks to Mr. Guild for the invaluable services which he has rendered to the Society during the past seventeen years. The vote of thanks was carried by acclamation.

The President announced that Dr. Allan Ferguson had been appointed Honorary Secretary for Papers, and heartily welcomed Dr. Ferguson in the name of the Society.

The following Papers were read :—

"Experiments with Mercury Jets and the Phenomena exhibited at their Impact with Steel and Glass," by Prof. WILL C. BAKER, M.A., Queen's University, Kingston, Ont., Canada.

"The Elastic Constants of Glass," by E. P. PERMAN and W. D. URRY, University College, Cardiff.

"A Valve-maintained High-frequency Induction Furnace and some Notes on the Performance of Induction Furnaces," by G. E. BELL, B.Sc., A.Inst.P., National Physical Laboratory.

A DEMONSTRATION of the Blowing of Selenium Bubbles was given by Major C. E. S. PHILLIPS, F.R.S.E.

May 11, 1928.

The following were elected Fellows of the Society: Elizabeth Mary Collins, B.Sc.; Norman Leslie Harris, B.Sc., A.Inst.P.

The following Papers were read :—

"The Amplitude of Sound Waves in Resonators," by E. G. RICHARDSON, B.A., M.Sc., Ph.D., University College, London.

"The Focus of a Gas-filled X-ray Tube," by R. E. CLAY, M.Sc.

A DEMONSTRATION of an Electric Harmonic Analyser was given by R. THORNTON COE, The British Thomson-Houston Co., Ltd.

May 25, 1928.

Special General Meeting.

The following resolution was proposed by Mr. R. W. PAUL, seconded by Prof. F. L. HOPWOOD, and carried *nem. con.* :—

"That the following words be added at the end of Article 37 of the Articles of Association of the Society: 'The Council, may, however, in its discretion, reduce or remit the subscription of any individual Fellow, in special circumstances.'"

Ordinary Meeting following the Special General Meeting.

The following were elected Fellows of the Society: W. H. J. Childs, K. L. Goodall, B.Sc. The President announced that the Council had elected the following to be Students of the Society: F. E. Hoare, W. Goldsmith, John J. Green, M. Farrell.

The following Paper was read :—

"Some New Methods of Linking Mechanical and Electrical Oscillations," by W. H. ECCLES, D.Sc., F.R.S., and Miss W. A. LEYSHON, B.Sc., Ph.D.

The meeting then adjourned to the Royal School of Mines, where a Demonstration of "Some Recent Studies in Alternating Magnetism with Some Possible Applications" was given by W. M. MORDEY, M.I.E.E.

June 8, 1928.

Special General Meeting.

The resolution passed at the Special General Meeting held on May 25, 1928, was unanimously confirmed.

Ordinary Meeting following the Special General Meeting.

The following Papers were read :—

"Contact Potential in the Dolezalek Electrometer Connected Idiostatically," by L. F. RICHARDSON, F.R.S., and STUDENTS of Westminster Training College.

"Some Experiments on the Light-Sensitivity of Commercial Selenium Cells," by GEO. P. BARNARD, The National Physical Laboratory.

"The Vapour Pressure of Water over Sulphuric Acid-Water Mixtures at 25°C. and its Measurement by an improved Dew-point Apparatus," by J. R. I. HEPBURN, M.Sc., Ph.D., Northern Polytechnic.

A DEMONSTRATION of a Simple Practical Application of the Properties of Selenium Cells was given by Mr. GEO. P. BARNARD, the National Physical Laboratory.

June 22, 1928.

The following Papers were read :—

"The Stability of a Valve Amplifier with Tuned Circuits and Internal Reaction," by R. T. BEATTY, M.A., B.E., D.Sc.

"The Scattering of Light by Particles of Metallic Oxides Dispersed in Dry Air," by T. C. NUGENT, M.Sc., and H. P. WALMSLEY, M.Sc.

"A Note on the Transmission of Cathode Rays through Thin Films," by B. L. WORSNOP, B.Sc.

A DEMONSTRATION of Various Methods for the Determination of Poisson's Ratio was given by J. P. ANDREWS, M.Sc.

July 7, 1928.

A visit was paid to the University of Bristol. The morning was devoted to a tour of the neighbourhood and to lunch. During the afternoon a meeting was held in the Henry Herbert Wills Physical Laboratory, and the following Papers were read in abstract :—

"The Mobility of Positive Ions in Air," by A. M. TYNDALL, L. H. STARR and P. A. SHEPPARD.

"The Polarisation of Impact Radiation in Mercury and Helium," (with DEMONSTRATION), by H. W. B. SKINNER.

"The Structure and Magnetic Properties of Single Crystals of Heusler Alloy," by H. H. POTTER.

"The Angular Distribution of Photo-electrons from a Single Crystal," by S. H. PIPER and H. W. B. SKINNER.

"A Method for the Measurement of the Gyromagnetic Ratio for Paramagnetic Substances," by W. SUCKSMITH.

The following papers were read in title :—

"Some Recent Developments of Statistical Mechanics" (lecture), by J. E. LENNARD-JONES.

"The X-Ray Analysis of the Fatty Acids and their Salts," by S. H. PIPER.

"Apparatus for the Determination of the Principal Magnetic Susceptibilities of Crystals at Low Temperatures," by L. C. JACKSON.

"An Integrating Photometer for Sun and Sky Light" (with DEMONSTRATION), by M. G. BENNETT.

A vote of thanks to Professor Tyndall and the Physics staff of the University, as hosts of the Society, was proposed by the President and carried by acclamation.

An exhibition of apparatus and experiments was then held and tea was served in the Laboratory.

XXX.—SOME NEW METHODS OF LINKING MECHANICAL AND ELECTRICAL VIBRATIONS.

By W. H. Eccles, *F.R.S.*, and W. A. Leyshon, *Ph.D.*

Received May 11, 1928.

Abstract.

The paper describes new arrangements for linking the vibrations of a tuning fork or quartz plate to the oscillations in an electric circuit. For this purpose use is made of various crystal contacts, of a neon tube, or of a pointolite lamp.

In a previous paper[1] an account has been given of a method of sustaining a tuning fork or quartz plate in oscillation by means of a neon tube flashing circuit, and in that paper it was shown that the mechanically vibrating body reacted upon the flashing circuit to such an extent as to keep the frequency of flashing constant over a wide range of the circuit conditions.

This method of maintaining tuning forks, quartz plates and the like in continuous oscillation is quite distinct in many respects from the well-known method employing a triode (or tetrode)[2]; and the steadying influence of the mechanical vibrator upon the concomitant electrical oscillations, which have made the thermionic method of importance in the laboratory and in engineering, is even more marked in the neon tube method than in the older method employing a triode (or tetrode). That this is to be expected is shown by B. Van der Pol in his papers[3] on "Relaxation Oscillations." The matter has also been discussed by one of the present authors in a recent paper.[4]

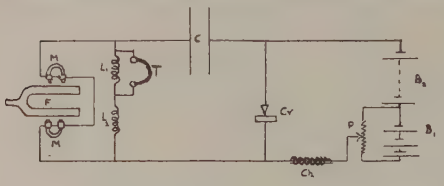
The present paper is concerned with a number of new methods of producing linked mechanical and electrical oscillations, some of which owe their properties to electrical conditions due to "relaxation" phenomena, but are often broadly described as due to "negative resistance."

Crystal Contact Method.

In 1910 one of the present authors demonstrated[5] to the Physical Society of London a crystal contact generating oscillations in an inductance coil and condenser connected across the contact. Almost any of the crystal combinations used as detectors in wireless receiving circuits could be used for generating oscillations over a wide range of frequencies, those of acoustic frequency being sufficiently energetic to be easily audible in a telephone. The frequency of the oscillations was found to depend principally upon the reciprocal of the square root of the product of the inductance and the capacity as was expected, but it varied somewhat erratically with the voltage applied and the condition of the contact. In 1924 these contact-generated oscillations were employed by Lossev[6] for receiving signals by the heterodyne method.

In 1926 and 1927 we attempted to apply contact-generated oscillations to the task of sustaining the natural vibrations of tuning forks or quartz plates. Fig. 1 shows one of the circuits arrived at after much experiment. Forks of frequency 512 and 2,000 have been successfully used in this circuit. In each case the

capacity of the condenser C was chosen so as to co-operate with the resultant inductance of its circuit to make the electrical oscillations generated by the contact of about the same frequency as the natural frequency of the free fork. It was



Cr. zincite crystal with steel cat-whisker—or needle-point.
C condenser.
L_1, L_2 inductances.
T telephone.
M, M telephone magnets.
F tuning-fork. P potential divider.
B_1, B_2 batteries. *Ch* choke coil.

FIG. 1.

found that the fork could be maintained in steady oscillation for several hours, and that the electrical oscillations, as perceived by aid of the telephones T, remained equal in frequency to that of the fork even when circuit alterations were made that would ordinarily take the circuit far out of tune. When the circuit was altered just too far, however, beats became audible in the telephones and the fork gradually came to rest. The steadiness of the arrangement may be illustrated by the fact that the whole experimental board may be carried from one room to another without stopping the vibrations.

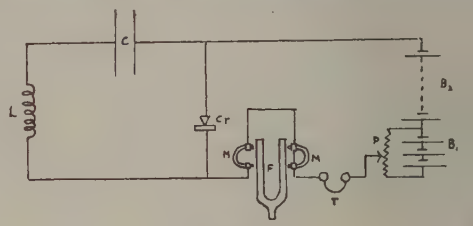
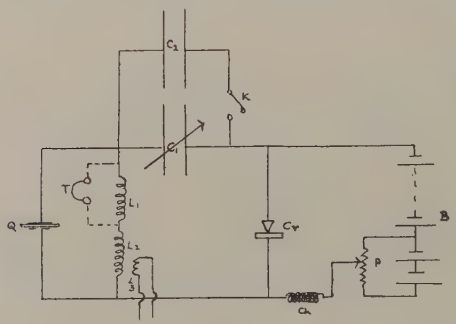


FIG. 2.

Another circuit which works well is shown in Fig. 2; in this the electromagnets of the fork and the telephones replace the choke coils of Fig. 1. When the capacity and inductance in the circuit of Fig. 1 are made sufficiently small, electrical oscillations of radio frequency are generated by the contact. The circuit can then be applied to maintaining the



Cr. zincite crystal and steel needle-point.
Q quartz "oscillator" crystal.
C_1, C_2 condensers.
K switch-key.
L_1, L_2 inductances.
L_3 coil coupling circuit to heterodyne wave-meter.
T telephones.
B battery.
P potential divider.
Ch. choke coil.

FIG. 3.

vibrations of a quartz plate, by which the tuning fork and its electromagnets are replaced. The circuit shown in Fig. 3 was used at first. The condenser C_1 was taken small enough to give the desired high frequency oscillations and the condenser C_2 was large enough to give an audible note in the telephones. Keeping

C_2 in circuit, a good working contact was found by trial while listening in the telephones; then C_2 was switched out of circuit. The high-frequency oscillations now being generated were detected and measured by aid of the heterodyne principle, an auxiliary oscillating wave-meter with its own telephones being employed. After gaining experience, it was found possible to dispense with the preliminary audio-frequency oscillations. In order to maintain a quartz plate in vibration it was placed at Q (Fig. 3) between electrodes connected to the circuit as shown. By suitable adjustment of the condenser C_1 the plate could be set in vibration. Once it started it reacted upon the circuit so as to force its natural frequency upon the whole circuit, and the heterodyne note heard in the wave-meter changed exceedingly little even when the capacity of the condenser was varied widely within limits. On passing either of these limits an abrupt change of frequency took place which was reproduced in the heterodyne note, and thereafter the latter followed continuously the variations in capacity. The quartz plate in use had a natural frequency corresponding to a wave-length of 2,320 metres; it could be satisfactorily sustained in vibration when the contact-generated oscillation was of wave-length 4,640 metres—an example of harmonic synchronisation.

In another example, with a different zincite crystal (now mounted in a crystal holder, with vertical steel needle substituted for the usual spiral cat-whisker) strong oscillations were obtained with B about 66 volts. In one region of this particular crystal, oscillations of wave-length 1,000 metres (300 kilocycles) could be obtained. A high resistance in series with the battery was found advantageous; the resistance actually used was a continuously variable "anode resistance" of the type used in resistance-capacity coupled amplifiers (0 to 100,000 ohms).

The quartz crystal (wave-length 2,320 m.) was placed either in the position shown in Fig. 3 or in parallel with the condenser C_1. In one experiment, with the crystal in the latter position, C_1 was altered until the quartz responded; it was then found that on continually increasing C_1 the heterodyne note heard in the wave-meter changed very little in pitch and then suddenly disappeared altogether. At this point, on leaving the crystal circuit unaltered and readjusting the setting of the wave-meter the heterodyne notes reappeared, a "silence point" being reached at about 2,500 metres. This gives some indication of the great range of control of frequency by the quartz.

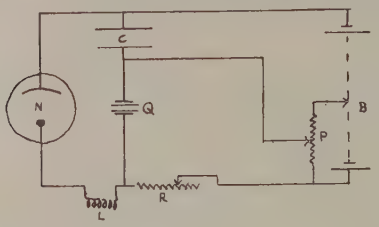
Neon Tube Method.

The method of maintaining linked mechanical and electrical oscillations by aid of a neon tube flashing circuit has already been described in the case when the vibrating body was a tuning fork. Here we may describe the application of the same method to maintaining the high-frequency vibrations of a quartz plate. A suitable circuit is shown in Fig. 4. As it is difficult to cause a neon tube to flash faster than, say, 30,000 times per second, the electrical circuits were chosen so that the rate of flashing was one-sixth the natural frequency of the quartz plate. In this case, as might be expected, the permissible range of variation of the circuit conditions is smaller than when the natural frequency of the mechanical vibrator is the same as that of the flashing phenomenon. As in the case of the tuning-fork controlled neon tube circuit, the control was most effective when the battery voltage was as low as possible and the series resistance of the critical value for flashing. It was noticeable that adding inductance to the circuit allowed the resistance to be reduced below its normal critical value.

Other Circuits.

(*a*) It has been found possible to obtain oscillations of audible frequency using the circuit shown in Fig. 5.

A battery voltage of 66 volts was used. A high note was heard in the telephones, increasing in pitch when C or R was diminished.* There was some



N neon lamp.
B battery.
P potential divider.
R high resistance.
Q quartz "oscillator" crystal.
L coupling coil.
C blocking condenser.

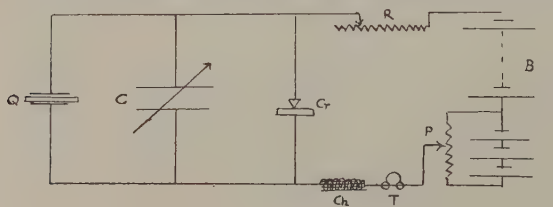
Fig. 4.

indication that this note was controllable in frequency by an associated quartz crystal.

(*b*) The circuit of Fig. 1 is with the omission of the tuning fork and its coils, the well-known circuit for sustaining electrical oscillations by means of an electric arc—the latter having been replaced by the zincite steel combination.

Using a "pointolite" lamp in place of the crystal combination, and with a suitable battery voltage and electric oscillatory circuit, it was found possible to maintain a tuning fork in oscillation.

(*c*) Using a tuning-fork controlled flashing neon lamp circuit, it has been found



C variable condenser
Cr. zincite-steel contact.
Q quartz "oscillator" crystal
R high resistance ($\rightarrow 100{,}000_{\omega}$).
B battery.
P potential divider.
Ch. choke coil.
T telephones.

Fig. 5

possible to coerce another circuit flashing at a frequency as much as seven times greater than the first by introducing into the circuit a voltage derived (through a transformer) from the first.

References.

(1) W. H. Eccles and W. A. Leyshon, The Electrician, p. 65 (July 16, 1926).
(2) W. H. Eccles and F. W. Jordan, The Electrician, p. 704 (June 20, 1919).
(3) B. van der Pol, Jahrbuch der drahtlösen Teleg. and Teleph., p. 178, Band 28 (1926).
(4) W. A. Leyshon, Phil. Mag., p. 305, Vol. 4 (1927).
(5) W. H. Eccles, The Electrician, p. 384 (Dec. 16, 1910). *See* also H. J. Round, Wireless World, p. 217 (Aug. 29, 1925).
(6) Lossev, Wireless World (Oct. 22, 1924).

* *See* also F. Seidl.

DISCUSSION.

Mr. T. G. HODGKINSON expressed great interest in the circuit arrangements which had been described. The mastery of the tuning fork over the natural frequency of the associated electric circuits must be attributed to the fact that the energy stored in the fork was very much greater than that stored electrically.

Dr. E. H. RAYNER suggested that if a copper oxide rectifier were used instead of a crystal it might be possible to maintain electric oscillations of considerable power.

Dr. W. H. ECCLES said that the most interesting feature of the circuits was one which it was difficult to demonstrate effectively to an audience—namely, the ability of the fork to impose its frequency on circuits of widely different natural frequency. The voltage-time curve in a neon lamp, arranged in association with a condenser to give intermittent illumination, tapers off in the neighbourhood of the cut-off, and the voltage decrements due to the fork are consequently able to introduce considerable changes into the time of discharge of the condenser.

XXXI.—CONTACT POTENTIAL IN THE DOLEZALEK ELECTROMETER CONNECTED IDIOSTATICALLY.

By L. F. Richardson, *F.R.S.*, and Students of Westminster Training College.

Received May 11, 1928.

Abstract.

It was found that the deflection x was related to the voltage V by the formula

$$x = k\{\tfrac{1}{2}V^2 + \eta V\},$$

k being constant from month to month, but η varying from 0·3 to 1·2 volts on different days. If it be desired to measure V it is therefore essential to reverse the polarity in order to eliminate η.

§ 1. The Main Asymmetry.

IT seems not to be generally mentioned in standard text-books that the original formula* for Kelvin's quadrant electrometer—namely,

$$\theta = k_1(A-B)\left(C - \frac{A+B}{2}\right)$$

is a bad misfit to the behaviour of a sensitive Dolezalek instrument when used idiostatically.† As θ is unchanged if A, B, C are each altered by the same addition we may write this classical formula in its simplest form if we state that

The potential applied to the vane is the conventional zero . . . . (1)

For then $$\theta = \tfrac{1}{2}k_1(A^2 - B^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which θ is the angle turned by the mirror, A and B are the potentials of the quadrants, and k_1 is an instrumental constant. For the idiostatic connection, either $A=0$, $B=V$, or else $B=0$, $A=V$, and in either event (2) becomes

$$\theta = \tfrac{1}{2}k_1V^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The following set of observations shows that the classical formula (3) is quite wrong in so far as it does not describe the important shift on reversing the sign of V.

Electrometer by Pye, No. 8646; quadrants lacquered black inside. Vane by Cambridge Instrument Co., looking like aluminium. Idiostatic connection.

Object connected.	Reversing switch.	Deflection from short-circuited reading.	Mean deflection. M	Shift on reversal. $\triangle$
		Cm.	Cm.	Cm.
Battery P ...	↑	9·22	6·46	5·52
...	↓	3·70		
Battery Q ...	↓	2·10	4·42	4·64
...	↑	6·74		

* Clerk-Maxwell, Electricity and Magnetism. Third edn., p. 339.

† There is a hint of it in Pidduck's Treatise on Electricity. Second edn., p. 127.

Values of k_1, calculated from other observations by formula (3), were found to vary widely, even changing sign at a certain voltage.

An obvious way of modifying (2) is to suppose that there is a contact potential η, so that we must write

$$\theta=\tfrac{1}{2}k_1\{(B+\eta)^2-(A+\eta)^2\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The scale deflection x is so nearly proportional to θ that by a change of constant from k_1 to k

$$x=\tfrac{1}{2}k\{(B+\eta)^2-(A+\eta)^2\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4A)$$

And as for the idiostatic connection, we have $A=0$, $B=V$; therefore

$$x=k\{\tfrac{1}{2}V^2+V\eta\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

On reversing, V becomes $-V$ and x becomes x', say, so that

$$x'=k\{\tfrac{1}{2}V^2-V\eta\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Hence,

the mean deflection, say M, $=\tfrac{1}{2}(x+x')=\tfrac{1}{2}kV^2$ . . . . . (7)

and the shift on reversal, say Δ, $=x+x'=2k\eta V$ . . . . . (8)

From (7) $$\frac{\text{E.M.F. of battery } P}{\text{E.M.F. of battery } Q}=\left(\frac{M_P}{M_Q}\right)^{\frac{1}{2}}=\left(\frac{6{\cdot}46}{4{\cdot}42}\right)^{\frac{1}{2}}=1{\cdot}20_9.$$

Measured by an electromagnetic voltmeter (Paul Unipivot) the E.M.F.'s were: P, 4·06 volts; Q, 3·36 volts; ratio, $1{\cdot}20_8$. Thus by reversing V and using means we obtain good agreement. To find η we eliminate k between (7) and (8), obtaining

$$\eta=\frac{V\Delta}{4M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

And combining this formula with the observations it is found that $\eta=0{\cdot}87$ volts from P, $\eta=0{\cdot}88$ volts from Q, the results agreeing as accurately as could be expected from voltmeter observations.

A better test of equation (7) is obtained by plotting M against V^2 in Fig. 1. Similarly, equation (8) is tested by plotting Δ against V in Fig. 2. The observed points lie close to straight lines through the origin, thus confirming the equations. The voltages for these diagrams were measured by means of a Rayleigh potentiometer and Weston cell, both of which had been standardised by the N.P.L. The electrometer was not that previously mentioned, but one by Griffin, having brass quadrants unlacquered inside; and the vane, by the Cambridge Instrument Co., looked like aluminium.

The most convenient way to find the contact potential η from these diagrams is to take the slopes of the lines. The slope of Fig. 1 gives $M/V^2=1{\cdot}68_8$ cm. volt^{-2}. The slope of Fig. 2 gives $\Delta/V=1{\cdot}98$ cm. volt^{-1}. Then, from (7) and (8)

$$\eta=\tfrac{1}{4}\frac{\Delta}{V}\cdot\frac{V^2}{M}=\tfrac{1}{4}\frac{1{\cdot}98}{1{\cdot}68_8}=0{\cdot}29_3 \text{ volt}$$

Observations of the type shown in Figs. 1 and 2 have been obtained on six occasions by students, and the graphs have always been found to be straight lines within the uncertainty of observation. On one occasion the (V^2, M) graph missed the origin, otherwise they all went through it.

§ 2. Other Asymmetries and Aberrations.

The importance of η is in the idiostatic connection. In the heterostatic connection η is usually small relative to A or B, and different asymmetries are conspicuous. Let us see whether any of these have complications with η. In heterostatic experiments, A/B is nearly unity, so that AB can scarcely be distinguished from $\frac{1}{2}(A^2+B^2)$ when they occur as factors of small correcting terms. The formula of A. H. and K. T. Compton* is not expressed in terms of *differences* of potential. Differences alone are actually effective. There is some doubt as to how it should be translated into the present difference-notation, but the following is a fairly inclusive form

$$\theta=\tfrac{1}{2}k_1(B^2-A^2)-AB(\lambda+\mu\theta+\nu\theta^3)-\tfrac{1}{2}(A^2+B^2)(\lambda'+\mu'\theta+\nu'\theta^3) \quad . \ . \ . \quad (10)$$

where λ, μ, ν, λ', μ', ν' are instrumental constants.

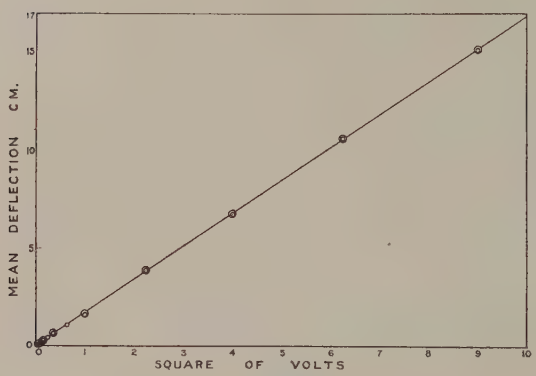


Fig. 1.†

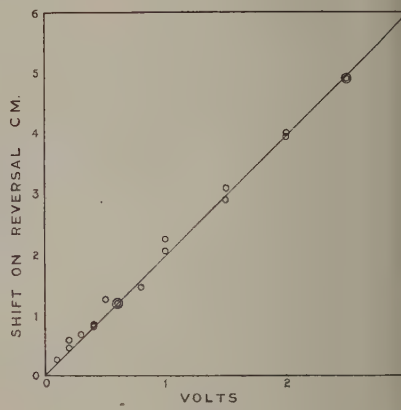


Fig. 2.†

Now to be general, let A and B have separate contact potentials α and β. Then (10) should be changed to

$$\theta=\tfrac{1}{2}k_1\{(B+\beta)^2-(A+\alpha)^2\}-(A+\alpha)(B+\beta)\{\lambda+\mu\theta+\nu\theta^3\}$$
$$-\tfrac{1}{2}\{(A+\alpha)^2+(B+\beta)^2\}\{\lambda'+\mu'\theta+\nu'\theta^3\} \quad . \ . \ . \ . \ . \ . \quad (11)$$

Experiment, however, shows that α is nearly equal to β, and that λ, μ, ν, λ', μ', ν' are not large enough seriously to disturb the measurement of η in the way already described. For the Pye electrometer aforesaid, this was seen, firstly, by joining the quadrants and applying various voltages, $A=B=V$. The deflection was nearly proportional to V^2, so that μ and ν were unimportant when $V<90$ volts. Also at 4 volts the deflection would be only 0·03 cm. when the quadrants were all joined. Secondly, to find whether it made much difference which pair of quadrants were at the same potential as the vane, the following observations were obtained on the Pye quadrants and Cambridge vane as before. The voltage was 4·072 throughout, being applied by four Weston cells in series.

* A. H. and K. T. Compton, Phys. Rev., XIV, p. 85 (1919 .

† The centre of a circle, regardless of its radius, marks an observation.

Date: 1928, May 5, 11h. to 13h.

Which quadrant terminal to vane.	Temperature near case.	M Cm.	Δ Cm.
Back	18·1	6·28	5·50
Front	18·5	6·44	5·51
Front	18·7	$6·45_5$	5·51
Back	18·8	$6·28_5$	5·53

It is seen that there is a slight asymmetry of M, but that it is only 1·3 per cent. of Δ.

Changing the potential of the case by 90 volts did not alter the deflection by 1 part in 1000.

Similar remarks apply to the Griffin electrometer.

The geometrical relation of x to θ is perhaps most conveniently included with internal aberrations due to slight imperfections in the form of quadrants and vane.

§3. Change of Contact E.M.F. from Day to Day.

The following Table shows that, whereas the sensitivity measured by M/V^2 remained steady to a few per cent. when the suspension was the same, yet η sometimes changed in a ratio as large as two in a few days. Change of humidity is suspected to be a cause of this.

Which quadrant terminal to vane.	Date. 1928.	MV^{-2} cm. volt^{-2}	η volt.	Room temp. °C.	Per-centage humidity in room.	Observers.
	Griffin quadrants, bare brass inside.			*Cambridge Inst. Co. Vane.*		
Front ...	Jan. 23 ...	$1·68_8$	$0·29_3$	7·7 to 10·6	Room colder for previous days	L. F. Richardson Figs. 1 & 2
	Jan. 25 ...	1·67	0·67	...	...	E. R. Collins and J. Dowson
	Jan. 26 ...	1·70	0·49	11·0	60	H. M. Gill and B. Ramsell
Front ...	May 3 ...	1·70	0·58	18·0	...	J. A. Cowell and A. H. Harper
Front Back	May 8	$1·64_8$ $1·65_7$	$1·18_8$ $1·19_5$	15·0	End of spell of hot, dry weather	L. F. Richardson
	(No. 1646) *Pye quadrants lacquered black inside.*			*Camb. Inst. Co.*	*Vane.*	
	Mar. 12 ...	$0·106_6$	$0·86_7$	...	...	W. Toyne
	Mar. 27 ...	new suspension.				
	Mar. 29 ...	$0·39_2$	$0·87_5$	...	...	L. F. Richardson Table I.
	April 27 ...	0·388	0·906	18·9	...	F. E. Blamey.
Front Back	May 5	0·390 0·379	0·871 0·894	19·0	...	L. F. Richardson
Front ...	May 21 ...	0·39	0·84	$13·0_5$	...	F. H. Brownridge and T. B. Cotton
Front ...	June 4 ...	$0·40_3$	$0·86_8$	$19·0_9$	93	S. O. Myers and D. J. Proctor.

The observations by students were in part supervised by Mr. R. S. Maxwell, M.A., B.Sc.

§ 4. Conclusion.

When a Dolezalek electrometer is used idiostatically it is most important to reverse the voltage and take the mean of the two deflections. Formula (5) is a good description, and (11), though presumably better, is perhaps unnecessarily elaborate. The contact E.M.F. η must be eliminated at the time, because it cannot be relied upon to remain constant for days. The mean is recommended, not on the rough principle "when in doubt take the mean," but as a clean elimination.

DISCUSSION.

Dr. Ezer Griffiths: I should like to ask the author whether he has made experiments to determine what factors may account for the changes observed in the values of the contact potential. In some experiments on the ionisation current for various applied potential differences between two aluminium electrodes cut from the same slab of metal I had trouble with contact potential effects, and found that heating one of the plates would produce marked changes. If one of the electrodes was heated and allowed to cool slowly a smooth curve relationship could be obtained between the contact potential and the temperature. The curve was not always reproducible, and after the electrode had cooled down to air temperature the value of the contact potential changed at a slow rate. Similar effects were observed with electrodes of other metals, such as zinc. In these experiments the electrodes were in an enclosure containing air dried with calcium chloride. Although the variations in the value of the contact potential were fractions of a volt, they were readily measured with the Compton electrometer. In view of the complexity of the phenomena, it would be useful to have the experiences of other workers who have encountered similar troubles.

Mr. R. W. Paul said that he had found it possible to eliminate contact potentials almost completely in the electrometer by making all the plates from the same piece of aluminium and baking them in a moist atmosphere.

Mr. G. L. Addenbrooke said that he had avoided contact potentials by using heavily gilded quadrants and a heavily gilded mica needle, aluminium not being employed. He had also designed an electrometer in which the conductors were made from the same piece of metal and brought to the same condition by heating and annealing. A double needle and eight quadrants were used astatically, and the deflection due to contact potential was thus reduced to 2 mm. or 3 mm. It depended on humidity, and was subject to long-period changes.

Dr. E. H. Rayner said that in his laboratory it was the practice to calibrate electrostatic voltmeters with alternating current. A Kelvin instrument with aluminium needle and brass quadrants was found to give a contact potential of about 0·36 volts, and the substitution of aluminium for the brass made matters worse. By careful attention to the condition of the surfaces the contact potential had been reduced to 0·05 or 0·15 volts, but it varied with the weather. It might conveniently be eliminated by the application of a correcting voltage to the quadrants.

Mr. A. P. Castellain said that at East London College it had been found that asymmetry of readings could be almost entirely eliminated by ensuring coincidence of the electrical zero (determined by joining the quadrants and applying a high voltage to the needle) with the mechanical zero. The asymmetry in a particular case amounted originally to 0·03 cm.

Mr. W. E. Benham said that as the electrostatic voltmeter was more often used for A.C. than for D.C., it was important to know to what extent A.C. readings would be affected by the errors discussed in the paper. The accuracy varied with frequency, the resistance and inductance of a silvered quartz suspension filament having appreciable effects at radio frequencies.

Dr. D. Owen: The Author's Paper serves a useful purpose in calling attention to the existence of the contact potential effect in quadrant electrometers used idiostatically. References to the effect and the necessity of allowing for it in steady voltage measurements are to be found in text-books, e.g., in Laws' "Electrical Measurements," and in Moullin's "Radio-Frequency Measurements." It will also be found that in all precision work in which the quadrant electrometer is to be used idiostatically workers are well aware of the existence of contact potential differences, and that instruments for use in alternate current measurements must be calibrated

with alternating voltages (*vide* Paterson and Rayner, Journ. I.E.E., 1913). Nevertheless, it appears to be true that the existence of this effect is not generally realised by electrical workers. These contact potential differences are puzzlingly indefinite, as may be seen by reference to a famous report by Sir Oliver Lodge to the British Association of 1884, entitled "On the Seat of the Volta Contact Electromotive Force in the Voltaic Cell." In some recent experiments on a new gold leaf electrometer one of my students, Mr. S. Ray, has observed a contact E.M.F. which varies from time to time, and which averages about 1·5 volts. These discrepancies vanish if the instruments are used for measuring alternating voltages, and it is preferable when small direct voltages are to be measured idiostatically to avoid the use of electrostatic instruments.

Dr. L. F. RICHARDSON : I communicated the Paper with some diffidence, expecting to be told that it was not new. The references mentioned by Dr. D. Owen will be useful. In reply to Dr. Ezer Griffiths, I suspect humidity to be a cause of the variation of η. Prof. Porter has chosen the Volta effect as the subject of his Presidential Address to Section A of the British Association, and we may expect further enlightenment on this question then. In reply to Dr. Addenbrook, Dr. Rayner and Mr. Paul, who have described processes for making η small, it is satisfactory to know that, even if they do not quite abolish η, yet η could be simply and accurately eliminated by reversing the polarity. In reply to Mr. Castellain, I would point out that 0·03 cm. is small in comparison with the 6 cm. mean deflection produced by the same voltage applied idiostatically. In reply to several speakers who were chiefly interested in alternating currents, the second member of equation (5) is proportional to the electrostatic couple when the vane is in equilibrium. When subject to an alternating E.M.F. the vane is not in equilibrium, except at two instants per cycle. But the classical theory, from which (2) is derived, when pursued further shows that the electrostatic couple is independent of the position of the vane ; and although this theory fails when A and B are large, yet it has been shown in §2 to be satisfactory for the idiostatic connection. Hence the equation of motion of the vane is

$$\theta = k_1\{\tfrac{1}{2}V^2 + V\eta\} + Id^2\theta/dt^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where t is the time and I is a constant times the moment of inertia. Integrating over a period of oscillation T, we have

$$\frac{1}{T}\int_0^T \theta dt = \frac{k_1}{2}\frac{1}{T}\int_0^T V^2 dt \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the term in η vanishing provided $\int_0^T V dt = 0$ . . . . . (14)

That is to say : Whatever the contact E.M.F. may be, the mean of the deflections for V and $-V$ applied steadily is the same as the mean deflection for an alternating E.M.F. of effective value V, provided that there is no resultant direct E.M.F. applied. Here (with reference to Mr. Benham's remarks) V is the potential at the foot of the suspension.

XXXII—SOME EXPERIMENTS ON THE LIGHT-SENSITIVITY OF COMMERCIAL SELENIUM CELLS.

By Geo. P. Barnard, The National Physical Laboratory.

Received May 8, *in revised form May* 25, 1928.

(*Communicated by* Dr. J. W. T. Walsh.)

Abstract.

Part I.—The Relation Connecting the Change in Conductance of Selenium Cells with Illumination.

As the result of an experimental investigation, it is shown that the change in conductance C due to a given intensity of illumination I is proportional to some power of the illumination I—i.e., $C \propto I^x$. The index value x varies from cell to cell, and is probably dependent on the construction of the cell. A sensitivity curve is given.

Part II.—The reaction of Selenium to Various Spectral Regions.

Some filter experiments are described in Part II, from which it appears that the change in conductance of selenium cells is dependent, not on the number of foot-candles incident on the cell, but rather on the amount of radiant energy received. Contrary to general belief, it is shown that, for the same amount of energy received, the action of the infra-red is relatively much weaker than that of some shorter wave portion of the spectrum.

Some experiments on the decay of conductance of selenium after exposure to radiation from various portions of the visible spectrum indicate that, throughout a large portion of the visible spectrum, the internal state of the selenium, as determined by the change in conductance, is independent of the wave-length of the exciting radiation.

A brief note on the nature of the light-action in selenium cells is added.

Introduction.

SINCE the discovery of the light-sensitive property of selenium in 1873,[1] selenium has been the subject of approximately 1600 articles, as well as of numerous patents.[2] Further, about 150 scientific papers have been published giving experimental data as to the light-sensitive properties of selenium. The results have been so contradictory and so marked with uncertainty that, so far, it has been impossible to establish by their means any theory of the action of light on selenium.

Empirical formulæ for the relation between the increase of conductance and the intensity of the illumination, purporting to represent the observations of different observers, range from the linear relation to the fourth-root law.

If C=the change in conductance due to illumination of intensity I, then we have

(1) $C=aI$ (Stebbins), where a is a constant.

(2) $C=aI^{\frac{1}{2}}$ (Rosse, Adams, Berndt, Fournier d'Albe),[3] where a is a constant.

(3) $C=aI^{\frac{1}{3}}$ (Hopius).[4]

(4) $C=aI^{\frac{1}{4}}$ (Rankine).[5]

In addition, we have the following empirical relations :—

(1) $R_a/R_b=(a/b)^n$ (Ruhmer),[6] where R_a and R_b are the values of the resistance under the smaller and brighter illuminations a and b respectively. The value of n was found to vary between 0·25 and 0·35.

(2) $C(C-b)=aI$ (Athanasiadis),[7] where I is the intensity of illumination, C the conductance and a, b are constants.

The wide differences in the empirical formulæ may doubtless be explained by differences in the time of exposure, range of intensity, colour temperature of the source; but the author has come to the conclusion that the discrepancies are, in a large measure, due to inattention to the conditions for accuracy in the measurement of conductivity and intensity, rather than to true physical differences in the quality of the cells exposed, arising from difference of construction.

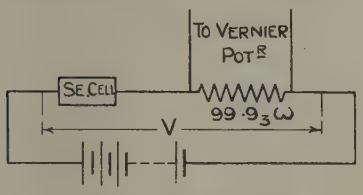


Fig. 1.—Test Circuit.

In the experiments here described great care was taken to attain as high a degree of accuracy as possible in the measurements, and it is suggested that this accounts for the consistency of the results now obtained. The measurements described in the paper have been repeated at intervals of several months, and are found to be quantitatively reproducible.

Part I.

Experimental Details.

The change in conductivity C of a number of selenium cells due to a given intensity of illumination was determined over the range 0-100 foot-candles. The source was a standard tungsten filament lamp mounted on a two-metre photometer bench. The colour temperature of the lamp was approximately 2290°K. By means of an electrostatic voltmeter, $100 \pm 0{\cdot}01$ volts were maintained across the lamp. The candle-power was then known to within 1/400. The cell under test formed part of the circuit shown in Fig. 1. The resistance of the standard shunt used for current measurement was 99·93 ohms; the fall of potential across this resistance was measured by a vernier potentiometer, so that the current flowing in the circuit was ascertained to within 2/10,000. The voltage across the selenium cell and the standard shunt was maintained at exactly 10 volts, as indicated by a calibrated voltmeter which could be read to within 1/1,000.

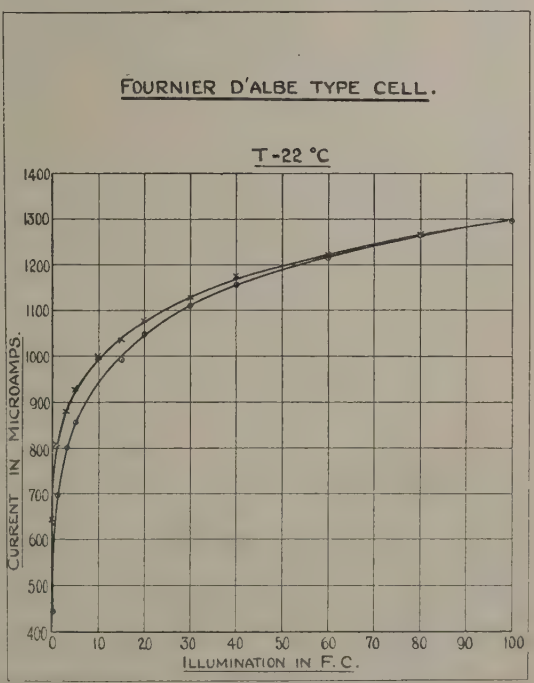


Fig. 2.—Current Illumination Curve for a Fournier d'Albe Type of Cell.

The "dark" current through the cell was first measured, thus giving the "dark" conductance $(1/R_0)$. A series of measurements was then taken with the cell exposed to illumination over the range 0-100 f.c. increasing, similar measurements being repeated with decreasing illumination. The measure of the ultimate change of conductance due to a given intensity of illumination may be conveniently defined as the total change of current resulting from the exposure of the cell to illumination. At each reading time was allowed (usually two to three minutes) for the current to attain a constant value, for, as is well known, the rise to maximum conductance of selenium when exposed to light occurs much more rapidly than the reduction to minimum conductance after the light is cut off. The change in conductance $(1/R_I - 1/R_0)$ due to a given illumination I was plotted against I.

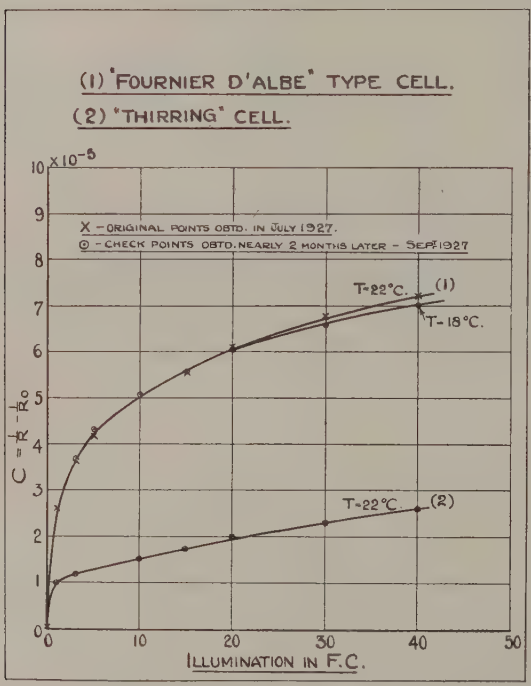


FIG. 3.—CONDUCTANCE-CHANGE ILLUMINATION CURVES.

The temperature of the cell was frequently noted. The necessity for this became evident in the course of later experiments on the temperature coefficient of resistance of selenium cells between 10-40°C., which showed that both the "light" and "dark" conductance increased linearly with temperature, whilst the change in conductance $(1/R_I - 1/R_0)$ due to a constant intensity of illumination I decreased linearly with temperature.

RESULTS.

As representative of the results, three curves are shown relating to two cells of widely different construction. In Fig. 2, representing observations on a cell of the Fournier d'Albe type, current is plotted against intensity of illumination; the well-known remanence effects of selenium are clearly evident. A similar curve was obtained for a cell of the Thirring type. In Fig. 3 the change in conductance C, of two cells (Fournier d'Albe type and Thirring type) is plotted against intensity of illumination I. In Fig. 4, log C is plotted against log I. The following formulæ fit the curves:—

(i.) Cell of Thirring type

$$C = 1{\cdot}63 \times 10^{-5} \times I^{0.390},$$

where I is measured in foot-candles and C in amperes $\times 10^{-5}$;

or

$$C^{2.56} \propto I.$$

(ii.) Cell of Fournier d'Albe type

$$C = 2{\cdot}80 \times 10^{-5} \times I^{0{\cdot}252}$$

I and C measured as above ;

or $$C^{3{\cdot}97} \propto I.$$

In Fig. 5 the sensitivity, defined as dC/dI, is plotted against I.

Experiments with different types of cells—i.e., cells of different make, have led the author to the conclusion that the change in conductance, under the conditions specified, can in every case be represented by a formula of the type

$$C = (1/R_I - 1/R_0) = AI^x,$$

where A is some constant, x being determined by a variety of conditions which

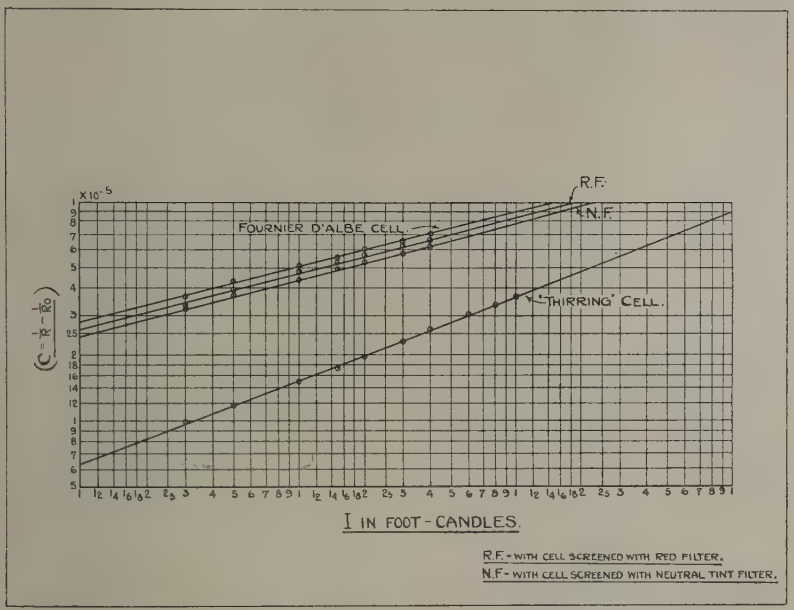


FIG. 4.—LOGARITHMIC CONDUCTANCE-CHANGE ILLUMINATION CURVES.

at present can only be approximately estimated. Although each cell has its own particular index value, this value, for the same cell, is found to persist even after a lapse of several months. It is to be noted that, even amongst cells of the same type, small variations of the index value occur. In general, no two cells of any one type have the same quantitative reaction towards a given intensity of illumination.

PART II.

The experiments described on the change of conductance with intensity of illumination were repeated on a cell of the Fournier d'Albe type with the cell screened (1) with a neutral tint filter, and (2) with a Corning red filter, the spectral transmission curve of which shows a fairly sharp "cut-off" at 6250 Å., with a mean transmission of 78·2 per cent. between 6400 Å. and 7100 Å. The results are shown

in Fig. 6. Plotting log C against log I, we see that C is still proportional to $I^{0.252}$ in both cases, although when the red filter was interposed the radiation incident on the cell was restricted to a very limited portion of the visible spectrum.

Considering the value of C corresponding to any particular value of I for the cell unscreened, we find that the effect of interposition of the neutral tint filter is equivalent to reducing the intensity of illumination by a mean value of 38·6 per cent. of the original intensity. Thus, according to the selenium cell, the transmission factor of this filter=61·4 per cent. Ordinary photometric measurements, however, gave the transmission factor as =12·0 per cent. This proves that the response of the selenium cell is not simply dependent on the number of foot-candles transmitted by the filter.

Similarly, ordinary photometric measurements gave the transmission factor

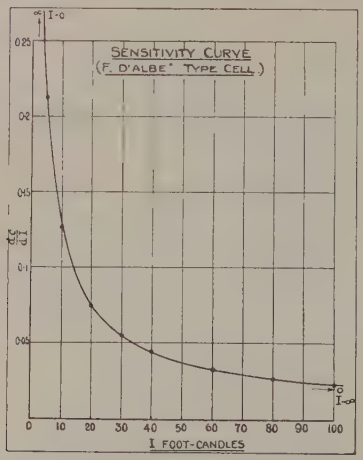


FIG. 5.—SENSITIVITY (dC/dI) ILLUMINATION CURVE FOR FOURNIER D'ALBE TYPE OF CELL.

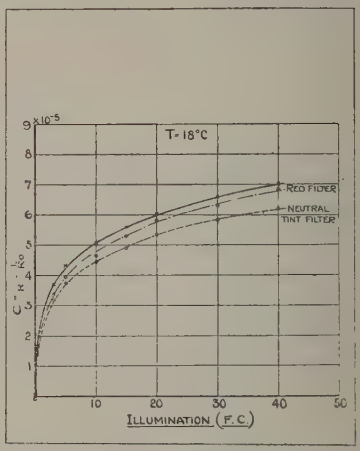


FIG. 6.—CONDUCTANCE - CHANGE ILLUMINATION CURVES FOR SCREEN CELL.

of the red filter as 11·45 per cent., whereas the effect on the selenium cell was that which would have corresponded to a mean transmission factor of 84·0 per cent.

A test was made with an infra-red filter which absorbed all radiation of a wave-length below 6800 Å. It was found that the effect on the conductance corresponded to a reduction of the intensity of illumination by an amount equal to 75 per cent. The spectral distribution of the source being practically that of a black body, Wien's radiation formula can be applied. It is found upon integration between the limits 7000-20,000 Å. and 4000-20,000 Å., and allowng for the infra-red energy absorption of the filter (approx. 10 per cent.), that the interposition of the infra-red filter only reduced the total radiant energy incident on the cell by a small amount. Thus the action of the infra-red upon the change in conductance of selenium is relatively much weaker than that of some shorter wave portion of the spectrum.

In the course of some experiments on the decay of the conductance of selenium after exposure to light the following tests were made :—

The cell was screened with a red filter and the tungsten lamp adjusted on the

bench until the steady value of C was equal, to, say, α. The illumination was then cut off and the change of C was plotted against the time t in seconds.

Exactly similar experiments were performed with the cell screened with blue, green and orange filters successively; at each test the tungsten lamp was adjusted to give the steady value of $C=\alpha$. The results are shown plotted in Fig. 7. It will be seen that, within the limits of experimental error, there is remarkable agreement between these colour-decay curves. Thus, although the steady value of $C=\alpha$ was obtained by exciting the cell with radiation from different spectral regions distributed throughout the visible spectrum, it appears that the effective result on the cell was the same in each case. The most natural inference to be drawn is that the internal state of the selenium was the same in each case.

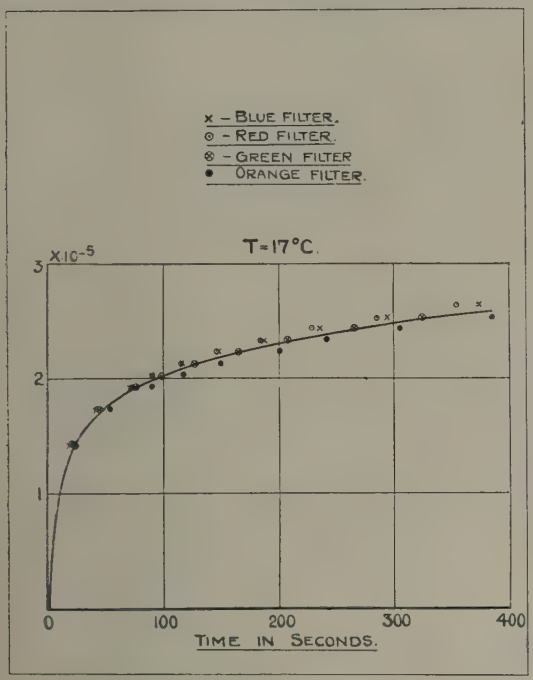


Fig. 7.—Conductance-change Time Curves for Screened Cell.

These results appear to conform with the general character of a curve recently obtained by Fournier d'Albe.[8]

Note on the Nature of the Light-action in Selenium.

Many theories have been proposed to account for the effect of light on selenium. On the whole, it cannot be said that our insight into the matter is very complete. Most recent investigators incline to the internal photo-electric theory in some form or other, the view being that light simply acts by liberating electrons. They endeavour to explain the inertia by assuming finite velocity of migration of these electrons. It is evident from the work of Gudden and Pohl[9] that the number of electrons which could be liberated by photo-electric action of the absorbed light according to the quantum equations are insufficient to account for the increases in conductance observed in selenium cells. Of course, it could be assumed that each primary electron liberated by photo-electric action of the absorbed light creates a sufficient number of secondary electrons; but experimental support is wanting for such an assumption. Moreover, any complete theory must not only account for the effects observed in light-positive selenium (increased illumination giving increased conductance), but also the inverse effects observed in light-negative selenium (i.e., increased illumination giving decreased conductance).[10] The author is inclined to believe that the effects are due to

crystalline structure. Brown[11] has shown that the sensitiveness of a selenium crystal varies upon application of mechanical pressure to the crystal. E. O. Dieterich[12] has shown how the resistance of selenium depends upon different annealing temperatures. Further investigators have demonstrated how the resistance of selenium cells depend on the voltage applied.[13] G. W. White[14] has shown that the resistance of selenium cells depend on the nature and pressure of the electrodes. It is therefore possible that there exists in the surface layers of the selenium a large number of bounding crystal surfaces in loose contact. The complete theory of the action of light on selenium is possibly intimately connected with the theory of coherer-action.

It is hoped later to continue these experiments with the object of assisting towards the elucidation of the nature of light-action on selenium.

ACKNOWLEDGMENT.

The author desires to express his very sincere appreciation of the kind encouragement and help of Dr. J. W. T. Walsh, and to thank Dr. D. Owen and Dr. M. A. F. Barnett.

APPENDIX.

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(14) G. W. White, Phil. Mag., Series 6, Vol. 27, pp. 370-81 (1914).

DISCUSSION.

Prof. A. O. RANKINE suggested that Fig. 3 was in danger of being misread in a sense unfavourable to the Thirring cell, since it contrasts the "light" current from such a cell with that from a Fournier d'Albe cell, whereas the proper test for the sensitivity of a cell is the ratio of "light" current to "dark" current. He was surprised at the reproducibility of the results in view of a factor not mentioned in the Paper—namely, the "voltage effect": if a steady E.M.F. greater than 1 volt be applied to a darkened cell, the resistance changes continuously with time. An even more important factor than precision of measurement in such investigations was the regulation of temperature, since the cell constant has a temperature coefficient of 5 per

cent. per degree. How had the author regulated and measured the temperature? Mr. Avery and the speaker had shown that the sensitivity is much increased if the cell be desiccated, and Prof. Thirring was now sealing his cells hermetically. The author was to be congratulated on his study (Fig. 6) of the dependence of the response on the quality of the stimulus.

Dr. D. OWEN, who had suggested the subject of selenium cells to the author, said that the latter was the first student member to read a paper to the Society, and offered him good wishes for his future work.

Dr J. W. T. WALSH said that the author's work was somewhat reassuring from the practical point of view of photometry and electrical engineering. Selenium cells had always attracted inventors, but their irregular behaviour was disconcerting and it was important to establish reproducible conditions.

Mr. T. SMITH asked whether the curves in Figs. 5, 6 and 7 had been drawn through observational points or derived by calculation.

Major C. E. S. PHILLIPS said that the most promising method of obtaining consistent results was to use selenium crystals of a definite character. An ordinary cell contains crystals soluble in water and its reliability can be much improved by boiling in this liquid. He had been able to make selenium crystals several mm. long; they could be spread into a thin layer without loss of light-sensitiveness. It was a curious fact that contact of metallic conductors with the crystals could be improved by working under oil.

AUTHOR'S reply: I should like to express my very sincere appreciation of Prof. Rankine's remarks. In reply, I desire to point out that Fig. 3 does not contrast the "light" current from a Thirring cell with that from a Fourner d'Albe cell in the sense implied by his statement. Fig. 3 contrasts the *extra* current through the two cells resulting from their illumination. It was not originally intended that Fig. 3 should give any information as to the ratio of "light" current to "dark" current for a given illumination for these cells, for the reason that this ratio has not been found to be a constant quantity for any one cell. At the commencement of the investigations it was thought that the "dark" resistance R_0 of any cell, measured under the conditions specified in the Paper, would not vary sensibly with age from the original "dark" value. This, however, was not so, since it was found that R_0 varied from day to day. Moreover, the "light" resistance R_I, corresponding to any given intensity of illumination, was by no means constant. But it was found that, provided the conditions of test were reproduced, the one constant quantity was the difference of the conductances $1/R_I - 1/R_0$. This is quantitatively reproducible for any of the cells examined, and is, as shown in Figs. 3 and 4, quite a definite function of the illumination. For example, the limits of variation of the "dark" resistance R_0 of the Fournier d'Albe cell, mentioned in the Paper, over the period of tests was $19{,}500^{\omega} - 22{,}500^{\omega}$, From the point of view of general interest, I give here values of R_0 and the corresponding values of R_I (for the cells exposed to 40 f.c.) for the 2 cells mentioned in the Paper:—

(1) Thirring cell: $R_0 = 366{,}800^{\omega}$, $R_I = 34{,}830^{\omega}$, $R_0/R_I = 10.5_3$.

(2) Fournier d'Albe cell: $R_0 = 22{,}420^{\omega}$, $R_I = 8{,}535^{\omega}$, $R_0/R_I = 2.6_3$.

The voltage effect mentioned by Prof. Rankine was duly considered. Prior to commencing the tests detailed in the Paper, an experiment was made to determine the variation of current through a cell, exposed to a constant illumination of 10 f.c., with the steady E.M.F. across the standard shunt and the selenium cell (Fig. 1) maintained at exactly 10 volts. In the extreme case, curiously enough, for the Thirring cell mentioned in the paper, the increase of current through the cell after 30 minutes was not greater than 1·0 per cent. of the value of the current flowing through the cell after 1 minute, a further 70 minutes giving a further increase of 3·4 per cent. Since the results expressed in Figs. 3 and 6 did not take more than 20 minutes to obtain, this effect was not considered to be serious. Moreover, part of the initial increase of current can be attributed to the extra current, flowing through the cell due to illumination, rising to a steady value. It was assumed that any error thereby introduced would appear in each test and be included in the cell constants. The consistency of the results appears to offer some justification for this assumption.

A separate investigation was carried out in order to determine the temperature coefficient of the cells examined, and in no case was a temperature coefficient observed as high as that stated by Prof. Rankine. The cells were placed in an electrical oven so arranged that they could be exposed to illumination, the source of which was also contained inside the oven. The surface of the inside walls, etc., of the oven was blackened. Any temperature desired between the

range 10°—40°C. was easily obtained and maintained for 2 hours to ensure that the cell was at the temperature of the enclosure. As typical of the results we may take the case of the Fournier d'Albe cell. The temperature coefficient of the "dark" conductance $1/R_0$ was +2·2 per cent. per degree centigrade over the range 10°—40°C., the temperature coefficient of the "light" conductance $1/R_I$ (with the cell exposed to a constant illumination of 58·6 f.c.) was +0·5 per cent. per degree centigrade, but the temperature coefficient of the change of conductance $1/R_I - 1/R_0$ due to a constant intensity of illumination was −0·5 per cent. per degree centigrade. Since I have expressed the results in terms of the change of conductance of the cells due to illumination, I had to contend with a possible error due to changes of temperature owing to the temperature coefficient of the change of conductance stated. It was not considered necessary to take any special precautions to regulate the temperature of the cell under test. Before testing, the cell was left in a darkened photometer room for 5-6 hours in order to ensure that the temperature of the cell was that of the room. During the period of the test the temperature of the room was not found to vary more than 0·2°C. The room-temperature was measured by a mercury-in-glass thermometer correct to 0·1°C. over the range used. There was not considered to be any serious heating of the cell due to the illumination during the time occupied by the test.

The cells examined were not hermetically sealed. Only in the case of the Thirring type of cell was any irregular behaviour observed, attributable to the presence of moisture films as suggested by Rankine and Avery* in their recent paper. It seems possible that Thirring cells are, from their construction, specially susceptible to trouble due to humidity, and in this connection it is interesting to note that Prof. Thirring is now sealing his cells hermetically.

I should like to record my appreciation of the remarks of Dr. D. Owen and Dr. J. W. T. Walsh.

In reply to Mr. T. Smith, the curve in Fig. 5 was derived by calculation, while the curves in Figs. 6 and 7 were drawn through observational points.

In thanking Major C. E. S. Phillips for his remarks, I should like to add that, in continuing the work with a view to assisting towards the elucidation of the nature of the light-action in selenium, I feel that observations should be made of the electrical, optical and mechanical behaviour of selenium crystals rather than of commercial selenium cells.

* Proc Phys. Soc., Vol. 39, p. 187.

XXXIII.—THE VAPOUR PRESSURE OF WATER OVER SULPHURIC ACID-WATER MIXTURES AT 25°C., AND ITS MEASUREMENT BY AN IMPROVED DEW-POINT APPARATUS.

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Abstract.

A critical study has been made of data previously used by Wilson in the construction of a mean curve for the vapour pressure of water over sulphuric acid-water mixtures at 25°C. The observations of Sorel (employed by Wilson over the concentration range 44-82 per cent. sulphuric acid) have been shown to be probably inaccurate, by calculations based on thermodynamics, and by determinations at 25°C., using an improved dew-point apparatus. The mean curve has accordingly been reconstructed, making use of the latest available data, and a set of most probable values for the vapour pressure has been compiled, taking into account the relative claims to accuracy of all investigators.

Introduction.

THE vapour pressure of water over sulphuric acid-water mixtures appears to be regarded as more accurately known than that over any other aqueous solution. The values at 25°C. are of especial importance, on account of the use of this temperature as a standard for purposes of comparison, e.g., in physico-chemical investigations concerned with ionic activity in solution ; it is, therefore, a matter of some importance that the most accurate data at this temperature may be available.

Wilson[1] has constructed a mean curve for the vapour pressure of water over sulphuric acid-water mixtures at 25°C., from the measurements of Regnault, Sorel, Helmholtz and Brönsted at temperatures in the neighbourhood of 25°C. ; he has also incorporated values obtained by means of a thermodynamic calculation, from the determinations of Burt, Sorel, Dieterici and Briggs, at other temperatures. He states that the mean curve thus obtained is probably accurate to within 0·1 mm. of mercury. The plan employed by Wilson consisted in plotting on a large scale, on the same graph, the results of the investigators before mentioned, and drawing a smooth curve to pass through the points so obtained. Mean values for the vapour pressure were read off at concentration intervals of 5 per cent., so that the curve might be reconstructed by other workers.

The author has made a critical study of the data and methods employed in this compilation and has arrived at the conclusion that Wilson's mean curve does not exhibit the most accurate values available. This view applies particularly to that portion of the curve relating to 40-60 per cent. sulphuric acid, over which range Wilson finds the graphical results in surprisingly good concordance. The author's criticism is based on the fact that Wilson makes extensive use of the data of Sorel, more especially over the range mentioned, whereas the work of subsequent investigators renders it probable that Sorel's figures are in error.

It is worthy of mention that the work of Smits and of Hacker, prior to 1921,

has apparently been overlooked by Wilson. Since 1921, Daudt, Grollmann and Fraser, and McHaffie have made further determinations, which serve to locate more accurately the two extremes of the curve, viz., for high and low concentrations respectively. An examination of Wilson's mean curve over these ranges reveals the fact that serious divergencies exist between the results of the separate investigators from which his data is drawn.

It appears to the author that exception may be taken to Wilson's method of compilation, on the score that he has given equal weight to the work of all investigators, irrespective of the relative degrees of accuracy attained or claimed in their work, and of probable errors due to defects in the method or apparatus used. In accordance with these views, a modified method of compilation has been adopted in this paper, by means of which a series of most probable values for the vapour pressure at 25°C. has been obtained.

Critical Discussion of Results Obtained by Earlier Workers.

In this section of the paper are given the results of an examination of the experimental methods employed by earlier investigators, in chronological order, and of criticisms made by later workers.

The method of Regnault[2] (1845) consisted in direct cathetometrical determination of the difference in level between the mercury in a normal barometer and that in one connected to a globe of 500 c.c. capacity containing the sulphuric acid-water mixture used. The difference in pressure so obtained was corrected for the pressure of air remaining in the globe (corresponding to approximately 0·1-0·2 mms. mercury). The temperature of the observations varied from 0-35°C. According to Tables given in the paper, the maximum error in the observations appeared to be of the order 0·3 mm. of mercury. Regnault's method has been criticised by Helmholtz, and later by Dieterici and by Daudt, who point out that the influence of the air remaining in the vapour space on the vapour pressure of water is ignored. Further, the author finds that when Regnault's figures, interpolated to 25°C., are plotted on a large scale against the concentration of sulphuric acid, the curve so produced is not continuous if the point corresponding to the mixture of concentration 52 13 per cent. sulphuric acid is included. A similar result obtains when the vapour pressures at 20° and 30°C. respectively are plotted against the concentration. The existence of this point renders the results of Regnault over the range 44-58 per cent. sulphuric acid of questionable value. If the point is disregarded and the curve made continuous, the values interpolated at concentration intervals of 5 per cent. are in moderately good agreement with those of other investigators, with the exception of the lower range (60-80 per cent. sulphuric acid), where the figures are undoubtedly high. (Table I, column 6.)

Helmholtz[3] (1886) determined the vapour pressure of water over three sulphuric acid-water mixtures, at temperatures between 0° and 50°C., by allowing air containing water vapour in equilibrium with the sulphuric acid-water mixture employed to expand adiabatically from a known pressure, in excess of atmospheric down to atmospheric pressure. The excess pressure employed was adjusted until a mist formed on lowering the pressure to atmospheric. The temperature depression was calculated from the initial and final pressures, the required vapour pressure of water being read off from vapour pressure tables for water. It may be noted

that the method is closely analogous in principle to the dew-point method, as described by the author. The accuracy of the results obtained is stated to be within 1 per cent. The author has not found it possible to make use of Helmholtz's data, as the figures obtained are too widely spaced for graphical interpolation. The results are in good agreement with those of later workers.

The observations of Sorel[4] (1889) were obtained by a dynamical method. A measured volume of dry air was passed through the sulphuric acid-water mixture used, and the weight of water vapour carried over was determined gravimetrically, applying certain correction factors. The observations covered a concentration range of 44-82 per cent. sulphuric acid, up to 95°C. The figures given in Sorel's table are quoted to an accuracy of 0·1 mm. only. Burt[9] has pointed out an important source of error in Sorel's method. Owing to the small quantity of acid employed, and the necessarily long duration of the experiment, the concentration of the acid-water mixture used becomes appreciably altered at the close of each determination. Further, Porter[5] has shown by thermodynamic methods similar to those of Wilson, and concerned with the calculation of the latent heat of evaporation of sulphuric acid-water mixtures, that Sorel's results are probably inaccurate. A comparison of the figures interpolated at 5 per cent. intervals from a large scale plot of Sorel's data with those of later investigators (Table I, column 7) shows that Sorel's results are consistently high.

Dieterici[6] (1893 and 1897) has carried out careful determinations of the vapour pressure of water over aqueous solutions at 0°C. ; he has pointed out two important sources of error in this type of work :—(1) The manometers previously employed were not sufficiently accurate for the measurement of low pressures ; (2) the pressure of air in the manometer may influence the results obtained. He, therefore, employed a differential tensimetric method, the manometer being closely analogous to that employed in the aneroid barometer. Differences in pressure were read off by means of a telescope and scale from the deflections of a small mirror attached to the corrugated metal box of the manometer. The accuracy of the observations is stated to be of the order 0·005-0·01 mm. of mercury. Wilson has recalculated Dieterici's results from 0°C. to 25°C., employing a thermodynamic method based on the approximate form of the Clausius-Clapeyron equation, the actual formula employed being :—

$$\text{Log}\ \frac{r_2}{r_1} = \frac{\Delta H_2}{2{\cdot}3.R} \cdot \frac{T_2 - T_1}{T_2 T_1} \quad \ldots\ldots\ldots \quad (1)$$

where r_1 and r_2 are the relative vapour pressures at the temperatures T_1 and T_2, and ΔH_2 the heat absorbed when one mole of water is removed from the solution without change in concentration. Values read off at 5 per cent. concentration intervals from a large scale plot of Dieterici's results, recalculated from 0°C. to 25°C., are given in Table I, column 9. They are in good agreement with those of later workers.

Smits[7] (1898 and 1902) has carried out very accurate determinations of the lowering of vapour pressure of water over sulphuric acid-water mixtures of low concentration (0-18 per cent. sulphuric acid) at 0°C. A micromanometer of special pattern, employing aniline and water, and similar in principle to the McLeod gauge, was used in these determinations. The results have been recalculated by the author from 0°C. to 25°C., making use of the thermodynamic method due to Wilson, and

are given in Table I, column 8. They are in excellent agreement with the direct measurements at 25°C. of Grollmann and Fraser.

Briggs[8] (1903) extended Sorel's observations, using the same experimental method as that employed by Sorel, up to 200°C. for concentrations up to 91 per cent. sulphuric acid. His results are open to the same objections as those of Sorel ; they have, however, been recalculated by the author from 100°C. down to 25°C., employing Wilson's formula, and are quoted in Table I, column 12. They are in good agreement with the direct measurements of McHaffie.

Burt[9] (1904) measured the actual pressure under which the sulphuric acid-water mixture boiled at different temperatures, ranging from 55°C. upwards. Porter found that Burt's data gave very regular results when employed for calculation of the latent of evaporation, and regarded them as much more reliable than those of Sorel. The author has recalculated Burt's figures for 75° and 100°C. down to 25°C., using formula 1 ; the results, when recalculated from each temperature, are in fair agreement amongst themselves and with those of other workers (Table I, column 11).

Brönsted[10] (1910) determined directly the vapour pressure of water over sulphuric acid-water mixtures at 20°C. and at 30°C. (*see* Table I, column 5). His results appear to have been obtained with great care, a modified tensimeter being employed in the determinations. Later workers (e.g., Grollmann and Fraser, Bennett) appear to regard the observations of Brönsted as the only earlier determinations for sulphuric acid-water mixtures which merit attention. Further, Grollmann and Fraser state that their results indicate the accuracy of Brönsted's measurements over the range 0-22 per cent. sulphuric acid to extend only to the first decimal place, and not to the third, as quoted.

Hacker[11] (1912) has carried out determinations of the vapour pressure of water over sulphuric acid-water mixtures, with the object of showing that the heat of dilution is variable with the temperature. A modified differential tensimetric method was employed, similar in principle to the Fortin barometer. The temperature at which observations were made ranged from 30-80°C. The results at 50°C. have been recalculated by the author to 25°C. ; the values given in Table I, column 13, have been obtained by interpolation at 5 per cent. concentration intervals from the recalculated figures. They are in fair agreement with those of other workers, except at concentrations 45 per cent. and 50 per cent. respectively, where they appear to be high.

The more recent determinations, subsequent to Wilson's Paper, include those of Daudt, Grollmann and Fraser, and McHaffie.

The measurements of Daudt[12] (1923) refer to sulphuric acid-water mixtures of high concentration (65-85 per cent.). A differential method for the measurement of small pressures (of the order 1 mm. or less), based on the variation of thermal conductivity with pressure, was employed. The maximum probable error is stated to be ± 4 per cent. (for pressures of the order 0·01 mm.). The author has recalculated Daudt's figures up to 25°C., employing formula 1 (Table I, column 11). They are in good agreement with the determinations of McHaffie over the same range.

Grollmann and Fraser[13] (1925) have made direct determinations at 25°C. of the difference between the vapour pressure of water over sulphuric acid-water mixtures of low concentration (0-22 per cent. sulphuric acid) and that over pure

Grams Sulphuric acid per 100 gms. solution.	§1. From determinations actually carried out at 25°C.			§2. By interpolation from determinations over a temperature range including 25°C.			§3. Recalculated, using Wilson's thermodynamic method, from determinations at :—						Most probable values.	Wilson's mean values.
							0°C.			75 and 100°C.	100°C.	50°C.		
	Grollmann and Fraser.	Author.	McHaffie.	Brönsted.	Regnault.	Sorel.	Smits.	Dieterici.	Daudt.	Burt.	Briggs.	Hacker.		
5	23·32	...	...	23·53	23·30	...	23·32	23·40	...	23·08	...	...	23·32	23·40
10	22·72	...	...	23·05	22·60	...	22·73	22·90	...	22·23	...	...	22·72	22·78
15	21·98	...	...	22·50	21·68	...	22·03	22·17	...	21·30	...	...	21·98	22·07
20	20·92	...	...	20·92	20·58	...	21·11	21·20	...	20·24	...	20·72	20·92	21·03
25	19·60	...	...	19·41	19·18	...	...	19·83	...	19·00	...	19·64	19·60	19·70
30	...	...	...	17·68	17·80	...	...	18·08	...	17·58	...	18·08	17·78	17·96
35	...	...	...	15·72	15·90	...	...	16·00	...	15·80	...	16·00	15·84	15·87
40	...	...	...	13·30	13·32	...	...	13·42	...	13·44	...	13·54	13·39	13·49
45	...	10·80	...	10·80	10·78	11·0	...	10·90	...	10·90	...	11·26	10·85	11·35
50	...	8.41	...	8·37	8·32	8·8	...	8·39	...	8·32	...	8·92	8·36	8·74
55	...	5·90	...	6·08	6·16	6·5	...	6·12	...	6·00	...	...	6·05	6·37
60	...	...	...	4·10	4·22	4·3	...	4·03	...	3·72	...	...	3·95	4·09
65	...	...	2·05	2·32	2·88	2·8	...	2·06	2·30	1·98	...	...	2·14	2·33
70	...	...	1·00	0·97	1·70	1·8	...	0·80	1·00	0·66	...	...	0·88	1·21
75	...	...	0·39	0·49	0·88	1·1	...	...	0·36	...	0·40	...	0·41	0·55
80	...	...	0·14	0·14	0·40	0·6	...	...	0·13	...	0·12	...	0·13	0·19
Col. No. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15

water. A very elaborate experimental method was adopted by these investigators making use of the Rayleigh manometer. Special precautions were taken to avoid previously recorded sources of error (e.g., presence of air in the apparatus). The authors state that they believe the measurements to differ from the true values by not more than 0·001 mm. Their results are recorded in Table I, column 2.

McHaffie's[14] (1927) determinations at 25°C. cover a concentration range of 65-80 per cent. sulphuric acid. A dynamical method was employed, according to which the water vapour contained in a measured volume of air, in equilibrium with the mixture, was condensed in a tube of known volume, immersed in liquid air. The condensed water was vaporised by raising the temperature to atmospheric and the pressure read off. The equilibrium pressure of water vapour at 25°C. over the mixture employed was calculated from the data so obtained. The results (Table I, column 4) agree closely with those of Daudt and of Briggs.

Method of Compiling Most Probable Values.

The results of all investigators are given in Table I. They have been classified as follows: Section 1 (Grollmann and Fraser, Author, and McHaffie) contains results of direct determinations at 25°C. Section 2 (Brönsted, Regnault, Sorel) gives figures obtained by interpolation from determinations over temperature ranges including 25°C. Section 3 (Smits, Dieterici, Daudt, Burt, Briggs, Hacker) contains figures recalculated from determinations at other temperatures. It seems probable that the figures of Section 1 represent the most reliable data, since, unlike the other figures, they are not liable to errors introduced through interpolation (Section 2) or extrapolation (Section 3). Of the figures of Section 2, those of Regnault and Sorel are probably not reliable, while those of Brönsted are regarded as reliable. Hence the author has not included the results of either Regnault or Sorel in compiling the most probable values for the vapour pressure. The figures of Section 3, being obtained by extrapolation, cannot be regarded as of the highest order of accuracy. However, as Wilson has shown, the factors which have to be applied in recalculating the relative vapour pressure from 0°C. to 25°C. are not so large as those for recalculating from 100°C. to 25°C. and therefore the error introduced by the extrapolation is probably smaller in the former case. This conclusion is confirmed by the agreement of the figures obtained with the direct determinations quoted in Section 1.

The results of Burt over the range 30-55 per cent. sulphuric acid are, however, in good agreement with those of other workers, and have been taken into account in obtaining the most probable figures over this concentration range, while those of Briggs are in good agreement with the figures of McHaffie and of Daudt.

The mean figures (Grollmann, and Fraser, Brönsted, Smits, Dieterici) of the vapour pressure for 0-25 per cent. sulphuric acid were found to be in close agreement with those of Grollmann and Fraser. Further, as already pointed out, the very careful observations of Smits and of Grollmann and Fraser appear to represent the most reliable figures over this range. The author has therefore adopted Grollmann and Fraser's figures exclusively as the most probable values for 0-25 per cent. sulphuric acid. The most probable values over the concentration range 30-60 per cent. sulphuric acid have been obtained by averaging the results of the authors Brönsted, Dieterici and Burt, which are in good agreement, while those for the

concentration range 65-80 per cent. have been compiled from the data of McHaffie, Daudt and Briggs, whose observations agree very closely.

The most probable values so obtained are set out in Table I, column 14, and are compared with the figures given by Wilson (Table I, column 15). The mean curve, constructed on a large scale from the most probable values obtained by this means, is found to be continuous, a circumstance which tends to confirm the accuracy of the figures. The divergencies between the author's figures and those of Wilson are not great until concentration 45 per cent. sulphuric acid is reached. At concentration 45 per cent. sulphuric acid, Wilson's figure is 0·50 higher than the most probable value; at concentration 50 per cent. sulphuric acid, the divergency is 0·38 mm., and at 55 per cent. 0·32 mm. Further divergencies occur over the higher range of concentration—viz., from 65-80 per cent.; Wilson's figure for 65 per cent. sulphuric acid is 0·19 mm. higher than the most probable value; for 70 per cent., 0·33 mm., and for 75 per cent. 0·14 mm.

The most serious divergencies between Wilson's mean values and those deduced by the author from the results of Brönsted, Dieterici and Burt were found to occur over the range 45-55 per cent. sulphuric acid. A fresh determination of the vapour pressures of water over sulphuric acid-water mixtures over this concentration range, therefore, appeared desirable, in order to locate accurately this part of the curve. It further appeared desirable to carry out the actual experiments at 25°C, in order to obviate errors introduced by interpolation. The author has accordingly carried out determinations at 25°C. of the vapour pressure of nine mixtures over this concentration range, using an improved dew-point apparatus. Details of the determinations are given in the experimental section. The results obtained are in good agreement with those of Brönsted, Dieterici and Burt. Table II shows the vapour pressures of the mixtures employed by the author, from the experimental results, and by interpolation from the figures of Brönsted and Sorel. The results of Sorel are in every case higher than those of the author, the maximum difference being 0·5 mm.

Experimental.

The dew-point method employed in the determinations was originated by Lescoeur,[15] and improved by Cumming[16]. (*See* also McBain and Salmon[17], Bennett[18].)

In preliminary experiments with Cumming's apparatus, difficulties were experienced through leakage. The liability of the rubber stopper to retain moisture introduced a further source of error. It was therefore decided to employ an apparatus made wholly of glass, with the exception of the dew-point tube. This apparatus (Fig. 1) consisted of a spherical bulb *A*, of 100 c.c. capacity, with two side tubes at the neck. The tube on the right led to a manometer *B*, via a cylindrical glass bulb, which facilitated filling and cleaning. The tube on the left connected with the vacuum tap *C*. This tap was designed so that the vapour space, including the tap bore, could be completely immersed in the thermostat tank, thus preventing condensation of vapour. The right-angle bend in the tap bore also minimised gas leakage through the tap. The neck (3 cm. in diameter) of the bulb was ground to fit the tube *D*, which was open at both ends. A silver thimble, identical with that used in Regnault's dew-point hygrometer, was cemented at the base of this tube.

The tube was fitted with a double-bored stopper carrying the thermometer *E* (graduated to 1/5°C.) and the tube *F*, which was designed as a combined gas bubbler and stirrer. All joints were lubricated with rubber-vaseline mixture of moderate viscosity. The apparatus was supported in a retort stand by a special clamp, which enabled it to be lowered into the thermostat tank and held firmly during experiments.

In order to surmount leakage difficulties in the first apparatus due to the cement used, a second apparatus was designed, consisting wholly of glass. This apparatus was brought into use before it was found possible to prevent leakage in the first glass apparatus. The essential feature of the second apparatus consisted in the substitution of a silvered glass tube for the silver thimble used in the first apparatus. Although Regnault, in his description of the dew-point hygrometer, points out the errors involved in Daniell's hygrometer, in which the dew formed on a glass bulb, he does not definitely state that the silver thimble employed in his apparatus is essential to the accuracy of the estimation. It therefore occurred to the author that a silvered glass surface (i.e., a surface on which a thin film of metallic silver has been deposited) might function equally well, provided that the thickness of the glass were not so great as to create a temperature lag from the inner to the outer surface. Thus, in Dines' hygrometer, a thin plate of glass or mica is employed to detect the formation of dew.

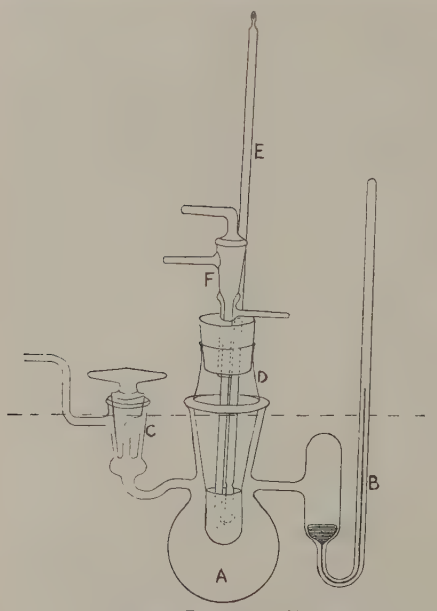

FIG. 1.—FIRST IMPROVED DEW-POINT APPARATUS.

In order to put this idea to the test, experiments were initiated on silvering glass test-tubes, which were substituted for the silver tube in Cumming's apparatus. After a number of trials, a suitable formula was found in which formalin is employed to reduce an ammoniacal solution of silver oxide. The formula quoted[19] was used, omitting the methyl violet specified. Each tube was thoroughly cleaned before silvering by immersion in chromic acid mixture for at least twenty-four hours. The results obtained with soft glass tubes were very satisfactory. The silver deposit took a high polish, superior, in fact, to that obtained with the tube of metallic silver, when rubbed up with chamois leather. The thickness of the glass tubes employed was 0·5 mm.

A form of Cumming's apparatus employed by the author, in which the tube of metallic silver was replaced by a silvered glass tube, was now used to determine the dew-point with a given solution of sulphuric acid. The result obtained, using a pressure of 3 cm. of mercury in the vapour space, was identical (within 0·05°C.) with that obtained using the tube of metallic silver. It appears, therefore, that a

silvered glass tube, provided that it is sufficiently thin, may be employed in the place of the silver tube of Regnault's dew-point hygrometer.

The second glass apparatus was similar in design to the first. The manometer (*B* of Fig. 1) was omitted, being replaced by a small U-tube manometer placed loosely inside the cylindrical bulb before evacuation. This arrangement allowed the vacuum to be tested, and at the same time considerably facilitated the cleaning of the apparatus after each determination, besides eliminating the possibility of mercury from the manometer entering the bulb. A cylindrical bulb (capacity 300 c.c.) enabled the silvered tube to be brought close to the observer. This was of some importance, since the apparent size of the silvered tube fell rapidly as the apparatus was moved away from the glass window in the side of the thermostat tank. The other parts of the apparatus were similar to those of the first, except that the section of the silvered tube was enlarged near the ground glass joint; the width of the neck was also increased. These precautions were taken to prevent the silvered tube from becoming contaminated, during removal between each experiment, through touching the greased side of the joint. The movable tap-joint of the bubbler tube (Fig. 1) was replaced by a sealed-in joint. This apparatus was successfully employed in two of the determinations recorded in Table II. The results obtained by its use were in agreement with those obtained using the first glass apparatus.

The Vapour Pressures of Sulphuric Acid-Water Mixtures at 25°C.

The sulphuric acid-water mixtures employed in these determinations were prepared in each case by admixture of pure sulphuric acid and water, and were standardised by titration against normal sodium carbonate solution. The standardization was carried out by determinations in triplicate, agreement being obtained within a limit of 0·05 per cent. This corresponds, in general, to a vapour pressure difference of 0·03 mm. of mercury.

The two improved forms of apparatus, previously described, were employed, the greater number of the observations being made with the first apparatus. Observation No. 7 (Table II) was made with both forms of apparatus, observation No. 3 with the second apparatus only.

Table II.

Solution No.	Percentage of sulphuric acid.	Dew-point °C.	Vapour pressure at 25°C. (mms. of mercury).		
			Author.	Brönsted.	Sorel.
1	41·81	14·50	12·38	12·34	...
2	43·79	13·35	11·49	11·33	11·7
3	45·04	12·40	10·80	10·71	11·0
4	45·59	11·95	10·49	10·38	10·7
5	47·46	10·40	9·46	9·48	9·8
6	49·45	8·70	8·44	8·57	9·0
7	51·45	7·30	7·67	7·66	8·2
8	53·24	5·35	6·71	6·85	7·3
9	55·23	3·25	5·79	5·97	6·4

Before use, the apparatus was cleaned by successive treatment with chromic acid, distilled water and alcohol, and finally dried by means of a current of hot air.

5 c.c. of the sulphuric acid-water mixture were run into the bulb, the tube affixed and the apparatus connected to a suitable pump. The pressure in the vapour space was reduced to that of 2 cm. of mercury, and no difficulty was experienced, using the rubber-vaseline lubricant, in maintaining this pressure over a period of 24 hours or more. The evacuated apparatus was supported in a constant temperature tank, which had a capacity of 30-40 litres, and was fitted with a large glass window. It was allowed to remain until equilibrium was reached ; in the case of the sulphuric acid-water mixtures a period of 30 minutes was found to be sufficient for this purpose.

The dew-point tube was half-filled with ether, and air drawn through by means of an aspirator. This method of cooling the tube was found to be very much superior to the hand-blower method recommended by Cumming ; it was also the method originally employed by Regnault in the dew-point hygrometer. The temperature was steadily lowered until a deposit of dew formed which could be clearly seen. The current of air was then caused to be less rapid, so that the temperature as indicated by the thermometer placed in the tube rose slowly. It was noticed in such preliminary observations that super-cooling occurred before deposition of dew, the first dew-point observed being lower than the following ones ; consequently, in all experiments a clearly observable deposit of dew was produced, and allowed to disappear, before taking observations of temperature. Experiment showed that, provided the temperature was not lowered to a point more than 0·5°C. below the dew-point, the point of disappearance of dew, with slow rise of temperature, was the same, whether the dew was deposited at the dew-point or at a temperature slightly below the dew-point. Using a highly-polished tube, it was found possible, within 0·05°C., to obtain the point of appearance of dew with falling temperature in agreement with the point of disappearance of dew with rising temperature. However, the first appearance of dew was difficult to observe, whereas the point of disappearance of dew was more readily perceived, and probably corresponded more closely to the condition that the vapour pressure of the dew on the cooled surface was equal to that of the vapour above the aqueous solution. Consequently, in all experiments, the point of disappearance of dew is quoted as the dew-point.

McBain and Salmon recommend a preliminary immersion of the lower portion of the silver surface in boiling water ; no dew subsequently deposits upon this portion, and the appearance of a line of division upon the bright surface is claimed to facilitate the observation of dew-point. These authors consider that the procedure mentioned is essential to the accuracy of determinations by the dew-point method. For the reasons given above, however, such preliminary treatment was judged to be unnecessary, and was therefore omitted in the author's experiments.

In every determination the observation of dew-point was carried out at least three times, allowing a period of 15 minutes to elapse between each observation for equilibrium to be re-established, and the determination was not accepted unless the three results agreed within 0·05°C. The results are shown in Table II. They have previously been discussed (page 255).

The Vapour Pressure of Water over Saturated Solutions of Sodium Chloride.

An independent comparison of results yielded by the dew-point and tensimetric methods appeared to be desirable ; the author has therefore examined that part of Landolt-Börnstein's tables which refers to aqueous solutions, with the object of

finding a modern reliable determination of the vapour pressure of water over a salt solution which might readily be reproduced. The work of Speranski,[20] on the vapour pressure of water over saturated solutions of salts appears to attain a high degreee of accuracy in tensimetric measurements. The author has interpolated Speranski's figures for the vapour pressures of water over saturated solutions of sodium chloride, at 20°C., 25°C. and 30°C., and has redetermined these figures, using the first modified dew-point apparatus previously described. The results are given in Table III.

TABLE III.

Temperature °C.	Dew-point °C.	Vapour pressure in mms. of mercury.	
		Author.	Speranski.
20	15·65	13·34	13·28
25	20·20	17·75	17·86
30	25·10	23·90	23·88

They indicate that the dew-point method is capable of yielding results in close agreement with those obtained by tensimetric measurements.

The glass apparatus employed was made by Messrs. Gallenkamp. The author desires to thank Dr. T. J. Drakeley, Head of the Department of Chemistry and Rubber Technology, Northern Polytechnic, for facilities provided.

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DISCUSSION

Dr. L. F RICHARDSON asked whether the percentages given in the paper represented the ratio of solute to solvent or of solute to solution.

Mr. J. H. COSTE said that the tables given by the author were most valuable since a good deal of industrial research is being conducted on the effects of moisture on various substances, and it is important to know to what surface tension they are being exposed.

The AUTHOR replied that a good deal of confusion existed in the literature between the two percentages referred to by Dr. Richardson. The percentages in the paper represented the ratio of the mass of sulphuric acid to mass of solution.

Capt. G. I. FINCH said that the definition of percentage used by the author represented the best chemical practice and it was important that it should be generally adopted.

XXXIV.—THE STABILITY OF A VALVE AMPLIFIER WITH TUNED CIRCUITS AND INTERNAL REACTION.

By R. T. Beatty, *M.A., B.E., D.Sc.*

Received May 19, 1928.

Abstract.

The paper gives algebraic and graphical methods for determining the conditions of stability for a tuned multi-valve amplifier.

I. Introduction.

THE stability of a valve amplifier is considered in this paper. The input, output, and intervalve circuits are tuned; the only mutual action between the circuits is that due to the capacity between the grid and the plate electrodes of each valve. It is found that the input grid admittance can be represented as a continued fraction with complex numbers from which a geometrical construction is derived which gives the input admittance at each stage. From this construction the *minimum* input conductance is derived in the form of a continued fraction with real numbers which can be summed stage by stage. In the special case of a *repeating amplifier*, the summation can be effected in general terms, giving the stability in terms of the valve constants and the repeating circuits in relation to the output load. When the output load is identical with the repeating circuits the formula is identical with that due to K. Posthumus,* but differs from that given by Hull† in that the phase angle of the repeating circuits at the limit of stability is found to be $-45°$ instead of zero.

List of Symbols in Practical Units.

ω	$2\pi \times$frequency in cycles/sec.
C_0	Grid-plate capacity of valve.
a_x	Reciprocal of valve differential resistance.
a_0	Grid-plate admittance of valve.
a_1	Output admittance.
a_n	Admittance of circuit between valves n and $n-1$.
$a_{g\,.\,n+1}$	Total grid input admittance at valve n.
g	Mutual conductance of valve.
$\sigma_{g\,.\,n+1}$	Total grid input conductance at valve n.

σ_{n+1}	t_{n+1}		Equivalent input circuit.
σ_n	t_n	conductance of / tangent of phase angle of	Equivalent circuit between values n and $n-1$.
σ_1	t_1		Equivalent output circuit.
σ_0	—		Grid-plate capacity.

T_n	$1+j\,.\,t_n$ $\qquad$ $(n+1)\ .\ .\ .\ 1$
R	H.F. resistance of a coil.
L	Inductance of a coil.
A	$a_0(g-a_0)$.
$\alpha_{n+1\,.\,n}$	$C_0\omega\,.\,g/2\sigma_{n+1}\,.\,\sigma_n$.
α_n	$C_0\omega\,.\,g/2\sigma^2{}_n$.
β	$\sqrt{1-4\alpha}$.
η	$\mathrm{Tan}^{-1}\,\sigma_0/C_0\omega$.

* Posthumus, Tydschrift van het Nederlandsch. Radiogenootschap, 3, pp. 106-112.

† Hull, Phys. Rev., 27, pp. 432-454 (1926).

II. The Input Admittance as an Operational Continued Fraction.

In a multi-stage amplifier (Fig. 1) each valve is represented as a generator with an admittance a_x in series; a_0 is the grid-plate admittance; a_1 is the output admittance, and includes the plate-filament admittance of the valve; a_2 a_3 . . . are the admittances of the networks between valves 1 and 2, 2 and 3 . . ., and include the grid filament admittance in each case.

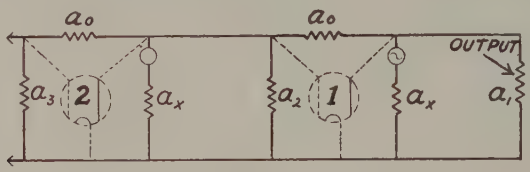

Fig. 1.

The plate load a_1 on valve 1 can be expressed as an equivalent grid input load on valve 1 by the method due to Miller* in the form†

$$a_0+A/(a_1+a_0+a_x),$$

where $$A=a_0(g-a_0).$$

Hence the total grid load on valve 1 is

$$a_2+a_0+A/(a_1+a_0+a_x),$$

and may also be considered as the plate load on valve 2; accordingly the equivalent grid input load on valve 2 is

$$a_0+\cfrac{A}{(a_2+2a_0+a_x)+\cfrac{A}{(a_1+a_0+a_x)}}.$$

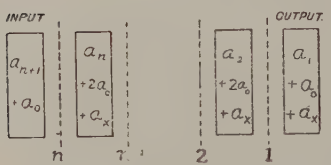

Fig. 2.

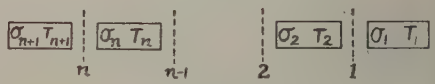

Fig. 3.

Hence the total grid input load at the grid of valve n is

$$a_{g\,.\,n+1}=(a_{n+1}+a_0)+\cfrac{A}{(a_n+2a_0+a_x)+\cfrac{A}{(a_{n-1}+2a_0+a_x)+\cdots\cfrac{A}{(a_2+2a_0+a_x)+\cfrac{A}{(a_1+a_0+a_x)}}}} \quad . \quad (1)$$

where a_{n+1} is the admittance of the network prefixed to valve n, and includes the grid filament admittance. The scheme in Fig. 1 may now be replaced by a set of equivalent circuits,† shown in Fig. 2, from which the equivalent total grid input at any valve can be found by the operations indicated in equation (1).

* Miller, Bull. Bur. Stand., 15, p. 367 (1919).
† Beatty, Phil. Mag., IV., p. 1085 (1927).

Since an admittance may be written as $\sigma[1+j\,.\,t]=\sigma T$, where σ is the conductance, t is the tangent of the phase angle, and T is evidently an operator, we may put

$$\begin{aligned} a_{n+1}+a_0&=\sigma_{n+1}\,.\,T_{n+1}\\ a_n+2a_0+a_x&=\sigma_n\,.\,T_n\\ &\vdots\qquad\qquad\vdots\\ a_2+2a_0+a_x&=\sigma_2\,.\,T_2\\ a_1+a_0+a_x&=\sigma_1\,.\,T_1, \end{aligned}$$

which gives a simpler notation for the equivalent circuits (Fig. 3). Equation (1) now becomes

$$\sigma_{n+1}\,.\,T_{n+1}+\frac{A}{\sigma_n\,.\,T_n+}\quad\frac{A}{\sigma_{n-1}\,.\,T_{n-1}+}\cdots\frac{A}{\sigma_2\,.\,T_2+}\quad\frac{A}{\sigma_1\,.\,T_1}\,.\quad\ldots\quad(2)$$

If we neglect a_0 in comparison with g, and assume that the grid-plate condenser has zero power factor we can write the approximate expression $A=j\,.\,C_0\omega\,.\,g$. On putting $2a_{21}=C_0\omega\,.\,g/\sigma_2\,.\,\sigma_1\ldots$ we may rewrite equation (2) in the form

$$a_{g\,.\,n+1}/\sigma_{n+1}=T_{n+1}+\frac{j\,.\,2a_{n+1\,.\,n}}{T_n+}\quad\frac{j\,.\,2a_{n\,.\,n-1}}{T_{n-1}+}\cdots\frac{j\,.\,2a_{32}}{T_2+}\quad\frac{j\,.\,2a_{21}}{T_1}\quad.\quad(3)$$

III. Graphical Representation of the Input Admittance.

T_1 is represented as a vector with one end moving along the vertical line in Fig. 4; the operation $j\,.\,2a_{21}/T_1$ is equivalent to $j\,.\,2a_{21}\,.\cos\theta_1\,.\,e^{-j\theta_1}$, where $\theta_1=\tan^{-1}t_1$,

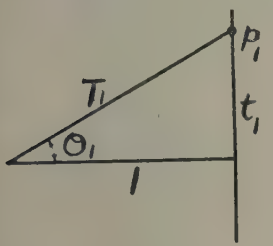

Fig. 4.

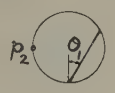

Fig. 5.

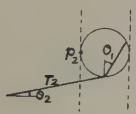

Fig. 6.

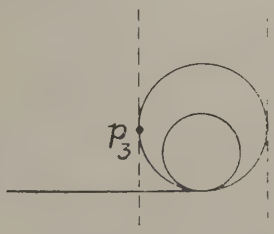

Fig. 7.

and this gives the thick line vector in Fig. 5, whose end moves on a circle of radius a_{21}. The operation is equivalent to inverting the vertical line t_1, and reflecting the circle so obtained by a line making an angle of 45° with the horizontal.

The vectorial addition of T_2 is shown in Fig. 6. It is seen that $T_2+j\,.\,2a_{21}/T_1$ is represented by a vector with one end fixed, while the other moves on the circle. As $T_2=1+jt_2$ varies, owing to variation of t_2, the circle suffers a vertical displacement, so that a doubly infinite set of vectors exists; each such vector terminates in the domain enclosed between the vertical dotted lines in Fig. 6.* The operation

$$\frac{j\,.\,2a_{32}}{T_2+}\quad\frac{j\,.\,2a_{21}}{T_1}$$

is performed in the same way as Fig. 5 is derived from Fig. 4, except that since the

* This is only true for small variations of ω, such as take place with tuned circuits, otherwise the diameter of the circle will vary owing to the occurrence of the quantity $C_0\omega$ in the expression for α.

domain between the dotted lines in Fig. 6 may be considered as composed of an infinite number of vertical lines each giving rise to a circle on inversion, an infinite number of coaxial circles will result. The limiting circles of the system are shown in Fig. 7, the radii are $\alpha_{32}/(1-\alpha_{21})$ and $\alpha_{32}/(1+\alpha_{21})$.

The geometrical interpretation of the subsequent stages is now obvious, and the stages are shown in Fig. 8. If the half breadth of any domain should exceed unity the input load may become a negative conductance, self-oscillation would ensue, and the construction would fail beyond this point. The minimum input conductance at the end of the chain is σ_{n+1} times the horizontal thick line in Fig. 8,

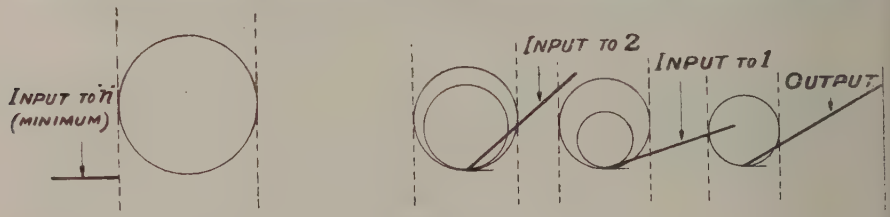

FIG. 8.

whose length is unity minus the half breadth of domain n—i.e.,

$$\sigma_{g\,.\,n+1}/\sigma_{n+1}=1-\frac{\alpha_{n+1\,.\,n}}{1-}\;\frac{\alpha_{n\,.\,n-1}}{1-}\cdots\frac{\alpha_{32}}{(1-\alpha_{21})}, \quad \ldots\ldots (4)$$

where all the terms are real. The value of $\sigma_{g\,.\,n+1}$ can thus be obtained by simple arithmetic in any particular case, and the amplifier is stable if $\sigma_{g\,.\,n+1}$ is positive.

IV. CONDITIONS FOR STABILITY WHEN THE LINKS OF THE CHAIN ARE EQUAL.

The case when all the valves and intervalve circuits are similar is of special interest; we put all the α's equal except the output term α_{21}, so that $2\alpha=C_0\omega\,.\,g/\sigma^2$ and $2\alpha_{21}=C_0\omega\,.\,g/\sigma\,.\,\sigma_1$ where σ is the conductance of any equivalent circuit lying between two consecutive valves, and σ_1 refers to the equivalent output circuit. Equation (4) now becomes

$$\sigma_{g\,.\,n+1}/\sigma=P/Q, \quad \ldots\ldots\ldots\ldots (5)$$

where
$$P=\frac{(1+\beta)^{n+1}-(1-\beta)^{n+1}}{2^{n+1}\,.\,\beta}-\alpha_{21}\left[\frac{(1+\beta)^n-(1-\beta)^n}{2^n\,.\,\beta}\right], \quad \ldots\ldots (6)$$

and
$$\beta=\sqrt{1-4\alpha}.$$

Q is of the same form as P, but with each power diminished by unity.

The relation between α and α_{21} to make $P=0$ is found by help of an auxiliary angle φ to be

$$\left.\begin{aligned}&\tanh\varphi=\sqrt{1-4\alpha}, \text{ when } \alpha<\tfrac{1}{4}\\ &\tanh\varphi/\tanh n\varphi=2\alpha_{21}-1.\end{aligned}\right\} \quad \ldots\ldots\ldots (7)$$

The corresponding relation when $\alpha>\frac{1}{4}$ is

$$\left.\begin{aligned}&\tan\varphi=\sqrt{4\alpha-1},\\ &\tan\varphi/\tan n\varphi=2\alpha_{21}-1\end{aligned}\right\} \quad \ldots\ldots\ldots (8)$$

The use of such terms as $\alpha_{n+1\,.\,n}$ each of which contains the product of the conductances of two consecutive circuits has simplified the notation, but physically terms of the form $\alpha_n = C_0\omega \,.\, g/\sigma_n{}^2$, each of which involves a single circuit, are more intelligible. We have $\alpha^2{}_{n+1\,.\,n} = \alpha_{n+1} \,.\, \alpha_n$, and the output term α_1 is given by $\alpha_{21}{}^2 = \alpha \,.\, \alpha_1$ in the case where all the intervalve α's are equal.

Fig. 9 shows the relation between α and α_1 according to equations (7) and (8)

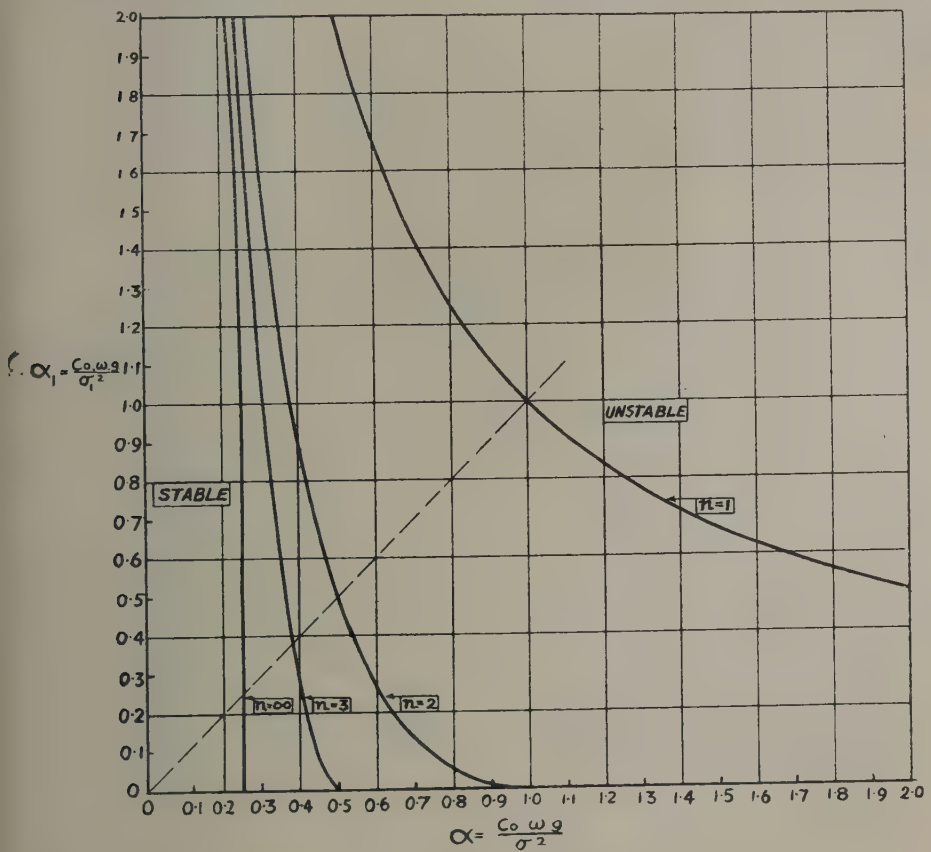

FIG. 9.

for an amplifier on the verge of instability. Curves are drawn for a one- two- three- and infinity-stage amplifier. For any given output load the critical value of α decreases rapidly at first as the number of stages increases and then more slowly. If

$$\alpha_1 < 1,\ \alpha = \tfrac{1}{4} \text{ for } n = \infty.$$

In the special case where $\alpha_1 = \alpha$ Posthumus* has obtained a solution in the form

* Loc. cit.

$4\alpha=\sec.^2\frac{\pi}{n+2}$, a result which follows easily from equations (8) of the present paper. Posthumus starts from the difference equation connecting the three potentials at the plates of three consecutive valves and expresses the result as a continuant which is formally equivalent to the continued fraction in equation (4). The values of α for various values of n are given in the following table and correspond to the intersection of the dotted line with the curves in Fig. 9.

TABLE.

n	$\alpha(=\alpha_1)$
1	1
2	0·500
3	0·382
4	0·333
⋮	⋮
∞	0·250

V. Discussion of Fig. 9.

As a numerical example take an amplifier in which each tuned circuit consists of a coil and condenser tuned to $\omega=10^7$: the H.F. resistance of the coil is taken as $42\,\Omega$ and the reactance of the coil as $1000\,\Omega$. Then the coil conductance is $R/L^2\omega^2=42\times10^{-6}$ mhos, and on adding the valve differential conductance assumed to be $0{\cdot}8\times10^{-5}$ mhos (the grid-plate condenser being supposed to have zero power factor) the conductance of the equivalent circuit is $(4{\cdot}2+0{\cdot}8)10^{-5}=5\times10^{-5}$ mhos. If $C_0=10^{-13}$ farads, $g=10^{-3}$ amps/volt, then

$$\alpha=10^{-13}\times10^7\times10^{-5}/(5\times10^{-5})^2=0{\cdot}4.$$

Fig 9 shows that if $\alpha_1=1$ the system will be stable for one valve but unstable for two; if $\alpha_1=0{\cdot}6$ a two-stage amplifier will be stable: if $\alpha_1=0{\cdot}2$ three stages will be stable. Since the output circuit is necessarily more heavily damped than the intermediate circuits we may put $\alpha_1<0{\cdot}4$, so that stability is to be expected with three stages.

If we take a better coil in which $L\omega=1000\,\Omega$, $L\omega/R=200$, and a valve in which $g=5\times10^{-4}$, $a_x=0{\cdot}8\times10^{-5}$ and in which C_0 has been reduced to $0{\cdot}2\times10^{-13}$ farads,

$$\alpha=0{\cdot}2\times10^{-13}\times10^7\times5\times10^{-4}/(1{\cdot}3\times10^{-5})^2=10^{-10}/1{\cdot}69\times10^{-10}=0{\cdot}59$$

so that stability is possible for two stages only.

VI. Result when the Power Factor of C_0 is Appreciable.

If σ_0 is not negligible so that $\alpha_0=\sigma_0+j\,.\,C_0\omega$ we find

$$A=j\,.\,C_0\omega\,.\,g\,.\,\sec\eta\,.\,e^{-j\eta},$$

where $\tan\eta=\sigma_0/C_0\omega$,

and consequently

$$2\alpha_{21}=C_0\omega\,.\,g\,.\,\sec\eta\,.\,e^{-j\eta}/\sigma_2\,.\,\sigma_1.$$

The result is that any circle as in Fig. 10 is rotated clockwise through an angle η

while its diameter is multiplied by sec η and the distance pq becomes $(1-C_0\omega \,.\, g \,.$ sec $\eta(1-\sin\eta)/\sigma_2 \,.\, \sigma_1)$. Under these conditions we must write in equation (4) $\alpha \,.$ sec $\eta(1-\sin\eta)$ instead of α. This value is always smaller than α so that the stability is increased by the introduction of σ_0.

For example, if $C_0=10^{-13}$ farad : $\omega=10^7$ radians/sec : $\sigma_0=10^{-6}$ mhos.

$$\tan\eta=\sigma_0/C_0\omega=10^{-6}/10^{-13}\times10^7=1$$

$$\therefore \quad \sec\eta(1-\sin\eta)=(\sqrt{2}-1)=0{\cdot}414.$$

Hence the condition for the stability of an infinite number of stages given by the bottom number in the table becomes $=\dfrac{0{\cdot}250}{0{\cdot}414}=0{\cdot}605$. In general the introduction of σ_0 increases stability with a corresponding decrease of amplification.

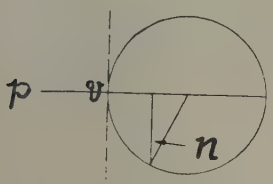

Fig. 10.

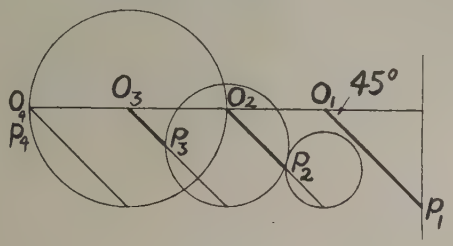

Fig. 11.

VII. Phase Angle on the Threshold of Instability.

In order that the amplifier should be on the threshold of instability the first condition is that the half breadth of the n^{th} domain should be unity : this condition does not fix the magnitude of the phase angles of the circuits. The second condition is that no thick line vector in Fig. 8 should penetrate into its corresponding domain, for if such penetration should occur at any stage it is evident from the method of formation of these vectors as given in Section III that all following vectors including the final one would also penetrate so that the final vector could not become zero. It may be seen from Figs. 4 to 7 that the point p_2 in Figs. 5 and 6 can only be obtained from p_1, in Fig. 4 if $\theta_1=-45$ deg. and that p_3 can only be obtained from p_2 if $\theta_2=-45$deg. Hence all phase angles must be -45 deg., that is, all circuits must be tuned to be inductive to the incoming signal.

Fig. 11 represents three stages on the verge of instability. The consecutive vectors are O_1P_1, O_2P_2, O_3P_3, and O_4P_4 which is zero. The radii of the circles are 0·382, 0·618, 1, and are calculated from the assumption that $\alpha=\alpha_1=0{\cdot}382$.

DISCUSSION.

Professor C. L. Fortescue : The elements of the amplifier as shewn in Fig. 1 are the same as those assumed by other workers and it is to be expected that the result given in equation (3) should be substantially the same as that obtained by others who have worked out the algebra of the circuits. Where Dr. Beatty has advanced our knowledge particularly is in the elegant graphical treatment given in Section IV of the Paper. But in this connection it is important to notice that the method is strictly limited to tuned-circuit amplifiers where the range of frequency under consideration is small. The graphical construction gives the limiting conditions

of stability and enables the frequency of the oscillations, where they break out, to be ascertained, but it does not give any indication of the voltage amplitudes at frequencies near that of the self-maintained oscillation. This is the important point in practice and it would be interesting to hear from Dr. Beatty whether the graphical construction can be adapted for this purpose with reasonable ease.

AUTHOR'S reply: No novelty is claimed for the relation given by equation (3) as regards its contents, but care has been taken to put it in a compact form which leads naturally to the subsequent graphical development; the use of admittance symbols instead of impedance symbols leads in this investigation, as in many others, to simple results. The analysis could have been performed in a different way by writing down a series of difference equations, each equation involving the potentials at the plates of three consecutive valves, and forming a continuant by elimination of these potentials; but the graphical method has the advantage of keeping the physics of the amplifier in view throughout the analysis. Moreover, it is possible that self-oscillations may occur in the output stages of an amplifier, while the early stages are stable. This condition would be indicated by the graphical method, which tests the stability step by step, but the continuant would indicate a stable system.

As regards the phase angles required for maximum voltage amplification, I doubt whether a generalised graphical construction can be given. I have given the result for two stages (Phil. Mag., IV, p. 1081), but for three stages the problem involves the maximum ratio between two lines drawn from a fixed point to a parabola, and in this form is incapable of geometrical solution.

XXXV.—THE SCATTERING OF LIGHT BY PARTICLES OF METALLIC OXIDES DISPERSED IN DRY AIR.

By T. C. Nugent, *M.Sc.*, and H. P. Walmsley, *M.Sc.*

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Abstract.

A cursory examination has been made of the time changes in the brightness of the tyndall-light from ZnO, CuO, CdO and As_2O_3 clouds. The changes found can be accounted for by supposing that the cloud particles disappear by aggregation and sedimentation. The curves obtained fluctuate in a similar way to the ionisation currents from the same cloud, as if aggregation produced unstable complex particles which periodically break up in large numbers. Evidence has been obtained that amicroscopic particles of cadmium oxide act as nuclei and collect cadmium oxide vapour during a condensation process. A series of clouds vaporised from various masses (m) of arsenic trioxide has been obtained in which the initial brightness of the tyndall-beam was approximately proportional to $m^{2/3}$. In certain clouds, the rapid fluctuations in brightness appear to form groups which succeed one another at intervals given by the formula $t=Ar^n$, where A and r are constants and n is an integer.

Theoretical.—I.

THE equations for the intensity of the light scattered by a spherical particle when placed in the path of a plane wave have been solved by Mie[1]. His formulæ have been used by Shoulejkin[2] to compute numerical values for the scattering when the particle is an ideal dielectric of refractive index 1·32. Shoulejkin finds that as the diameter d of the particle increases there is a smooth continuous change from the scattering of light according to Rayleigh's law to its reflection and refraction as given by Fresnel's equations. When $d \gtrsim \lambda/3$, where λ is the wavelength of the incident light, the scattered energy closely obeys Rayleigh's law, and at right angles to the incident beam the scattered light is practically plane polarised. As d increases the polarisation becomes less complete. For values of d greater than the general character of the distribution of dispersed energy does not change greatly. It approximates closely to that given by the ordinary laws of reflection and refraction. The results for $d \gtrsim \lambda/3$ seem in close accord with Mecklenburg's[3] experiments with sulphur sols, particularly for $5\mu\mu < d < 100\mu\mu$.

Thus, if a quantity of matter C is dispersed into n spherical particles, and $d \gtrsim \lambda/3$, the intensity I of the laterally scattered light varies as nd^6. But C varies as nd^3, whence

$$I = RCd^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At the other limit, the total surface of the particles varies as nd^2, so, as a surface reflection effect

$$I = R'C/d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where R and R' are constants.[4]

Tolman[5] finds with silica suspensions that (2) is closely obeyed down to $d = 997\mu\mu$.

It seems legitimate to assume from the above that the relation between I and d when C is constant will be represented by a smooth curve, approximately given

by (1) and (2), at the limits, and possessing a single maximum roughly near $d=\lambda$. This shows that if a cloud of uniform spherical primaries coagulates, the secondaries also being spherical, the intensity of the tyndall-beam will alter with time (t). The $I-t$ curve will depend upon the law of coagulation, but it seems reasonable to suppose that when the primaries are very small it will be somewhat similar in shape to the previous curve, and that in practice we should obtain the whole or part of this curve according to the size of the initial particles.

The experimental curves to be described will be interpreted on the assumption that their theoretical $I-t$ curves, when coagulation occurs, are of this shape, although X-ray analysis has shown that the particles employed are crystalline. Since there seems nothing to hinder their formation from vapour, they are probably faceted—i.e., we are dealing with tiny crystals and crystal aggregates. It is further assumed that as coagulation proceeds the fraction of light which is polarised decreases. The initial polarisation for spherical primaries of $d \ll \lambda/3$ will be almost perfect; but, judging by Gans [6] results for ellipsoidal particles, it is to be expected in our case that, even when $d \ll \lambda/3$, the polarisation will only be partial.

Anticipating the experimental results, the $I-t$ curves observed conform with these assumptions. It is found, however, that they are not smooth, but fluctuate[7]. In many cases the magnitude of the fluctuations seems too great to be attributed to observational error. Suppose coagulation is causing a general diminution in scattering. A subsequent increase in brightness must be due to an increase in the number of particles in the element of cloud (about 1 c.c.) on which observations are made. If the cloud is homogeneous in the sense that the element is representative of the cloud, this must arise from the disintegration of unstable aggregates. If, however, it is due to heterogeneity, resulting perhaps from imperfect mixing, little change should occur in the percentage of polarised light which is scattered. As this depends on the degree of dispersion, it should however increase if disruption of aggregates takes place. When, therefore, the brightness and the polarisation fluctuate collaterally, the effect has been interpreted as indicating that the increases in the number of particles from disruption periodically outnumber the decreases due to aggregation.

Experimental.—I.

The apparatus employed for dispersing the clouds and for measuring the ionization currents from them has been described previously[10]. The photometric measurements were made upon a sample of the cloud which was withdrawn from the 850 litre cistern, and introduced into a slightly modified form of the tyndallmeter described by Tolman and Vliet[8], the brightness of the scattered light being measured with a Macbeth illuminometer.

The light scattered laterally by clouds dispersed by arcing between metallic electrodes was found to be coloured. That from copper electrodes was deep blue, zinc gave a bluish green colour, whilst lead cadmium and tin gave bright green clouds. The light from a cloud produced from cadmium when examined with a spectroscope showed a continuous spectrum from the blue to the green. The yellow and red end of the spectrum seemed totally absent. Although the blue colour is similar to that found by Tyndall with clouds produced by photo-chemical reactions, the clouds behave differently on ageing. Tyndall[9] found that his clouds altered with time, and ultimately became white. With the clouds from the arc there was no marked

visible change in colour with time. The light was found to be partially polarised, the plane of polarisation containing the incident ray and the line of sight. For the photometric measurements, a nicol prism was attached in front of the eyepiece of the illuminometer, and the intensities of the maximum and minimum transmissions were measured throughout the experiments (curves *A* and *B* in the graphs).

In taking the observations it was found that if, at a given time, the fields of the Lummer-Brodhun "cube" were adjusted for equality of brightness and left, the brightness of the tyndall-light fluctuated fairly rapidly about the standard. This fluctuation seems superposed upon the general change in brightness as the cloud ages. As it was evident that all the changes in brightness could not be recorded, the following procedure was adopted: Five settings for the stronger component were read alternately with five for the weaker. The times of the first and last reading of each set of ten were noted. Their mean was taken as the "time of observation," and the means of each set of five readings were taken as the values of the components at the time of observation. This method of reducing the observations tends to eliminate the more rapid changes in the light values.

Since the period (approx. 2 mins.) occupied in recording the ten settings is approximately equal to that required to make a measurement of the ionization current, it makes the results more comparable with the conductivity measurements. The point is illustrated by Fig. 5, where an attempt has been made to plot the individual readings for the stronger component of a cadmium oxide cloud. The readings are joined by straight lines. The smooth curve passes through the means of sets of five observations. The former curve more closely represents the actual changes in brightness which occurred than the latter, which gives only the general trend of the phenomena.

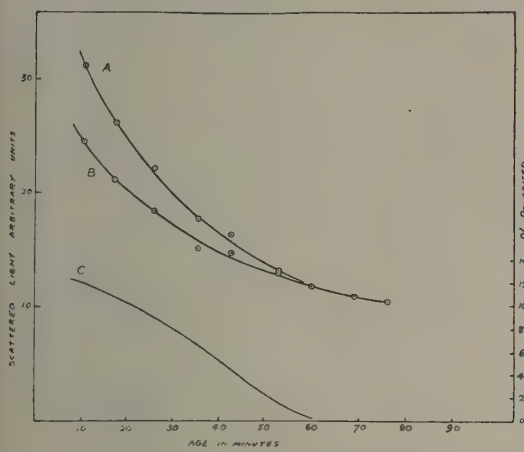

FIG. 1.—ZINC OXIDE.

The results of typical experiments on clouds dispersed from an electric arc are shown in Figs. 1 to 6. In no case was the scattered light completely plane polarised, as it should be if the scattering conformed with Rayleigh's formula. Thus the diameters of the cloud particles are either not extremely small compared with the wavelength of the incident light or they are not spherical in form. The colour of the scattered light shows that very few of the particles can have diameters greater than the wavelength of light, since they are evidently not sufficiently numerous to reflect from their surfaces the colour characteristic of the disperse phase in bulk. The colour and polarisation of the scattered light, therefore, show that the clouds consist mainly of ultramicroscopic particles.

Zinc Oxide Clouds.

Fig. 1 shows the curves which were obtained from a comparatively dense cloud from a zinc arc. Since the curves ultimately unite, the polarised light ultimately disappears; showing that the average size of the particles has increased, and hence that aggregation has taken place. The decrease in A and B with age indicates, therefore, a gradual decrease in the number of particles per unit volume which must be due to loss by aggregation or sedimentation.

Fig. 2 is due to a weaker cloud of zinc oxide particles produced by a silent arc. The general shape of the curves A and B is what one would expect from the coagulation of particles whose initial dimensions are small compared with the wavelength of light. The average size of the particles should be increasing whilst the scattering is passing through the maximum. This seems the case, for the percentage polarised diminishes steadily during the first 25 minutes. Sedimentation and further aggregation will account for the subsequent loss shown by A and B.

Sedimentation should have no effect on the polarisation of the scattered light, unless it alters the composition of the cloud. When particles of varying sizes are present, the larger particles are more likely to be precipitated than the smaller. As the latter scatter a larger proportion of polarised light than the former, continued sedimentation in such a cloud will tend to increase the percentage of polarised light scattered. So long as the effect of growth in size by aggregation is greater than that due to sedimentation, the percentage of polarised light will diminish; but, as the rate of aggregation diminishes with age, the loss of the larger particles by sedimentation may predominate, and cause the percentage to increase. The joint effects of continuous coagulation and sedimentation will in general produce a smooth curve for the percentage possessing a minimum. Neglecting the fluctuations, this is the general shape shown by curve C.

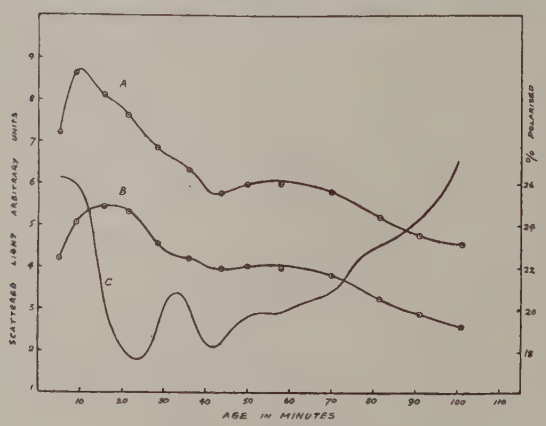

Fig. 2.—Zinc Oxide.

Copper Oxide.

Fig. 3 shows the curves obtained from a cloud produced by passing a current of 5 amperes across a copper arc for 15 minutes. The percentage of polarised light is considerably greater than before. The variations with time of the total scattering and the fraction polarised are oscillatory, the maxima for each curve occurring approximately simultaneously. Apparently at these times a reversal of the process of aggregation is taking place—i.e., the aggregates in the cloud are breaking up at a rate greater than their rate of production. The high percentage of polarised

light points to a high degree of dispersion in the cloud, and this seems supported by the relatively slight fall of the percentage on the whole. The much more rapid decrease in the total scattered light would indicate that the loss of particles is very largely due to sedimentation.

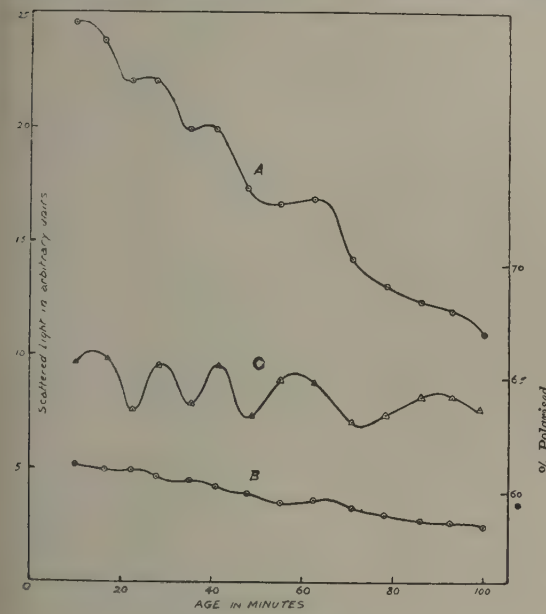

FIG. 3.—CUPRIC OXIDE.

CADMIUM OXIDE.

Most of our experiments were carried out on clouds from cadmium electrodes, and Fig. 4 gives a set of curves frequently obtained. The scattered light is green, and shows small fluctuations as its intensity diminishes with age, the most marked in this cloud occurring after 15 minutes. From the colour and high percentage of polarised light, the degree of dispersion seems fairly high. The general fall in intensity with age indicates the loss in number of the particles by coagulation and settling, and the fluctuating percentage seems to indicate that unstable aggregates are formed during the coagulation process, which break up periodically in large numbers. Fig. 5 shows for the early stages of this cloud the actual observations and the means from which Fig. 4 is drawn. The ionization current *D* was obtained with 400 volts on the collecting condenser. The rapid fall to 15 minutes is due mainly to recombination. The subsequent rise is due to the production of charges in the cloud. It will be noticed that as the percentage curve passes through maxima and minima, collateral changes occur in the current. From electrical considerations, the increases in current strength have been attributed to the

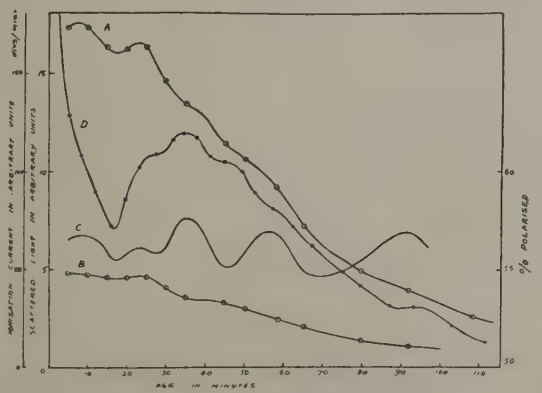

FIG. 4.—CADMIUM OXIDE.

disruption of aggregates in the cloud.[10] The explanation offered for the increases in the polarisation is the same, so the curves seem corroborative.

Fig. 6 shows the behaviour of another cadmium oxide cloud. The initial distribution of number and size amongst the particles makes the total scattering and the percentage polarised roughly the same here as in Fig. 4, but the percentage, instead of remaining fairly constant, falls rapidly and vanishes after 50 minutes. At 20 minutes the total scattering is again equal for both clouds, but the percentage polarised is considerably less in Fig. 6. At this time the average size of the particles is therefore greater in Fig. 6 than in Fig. 4, so their number must be less. Again, the greater rate of fall in the polarisation in Fig. 6 shows that coalescence of the responsible particles has been more rapid than in Fig. 4—i.e., their collision frequency has been greater. From the initial similarity of the clouds, the greater average size of the particles at 20 mins. in Fig. 6 cannot be due to the aggregation of larger primary particles. It must arise from a greater initial volume density of particles. These scatter slightly less total light than the corresponding particles of Fig. 4, so their average size must be smaller. Such particles alone would scatter a higher percentage of polarised light than those in Fig. 4. Hence, in Fig. 6, we must have initially a number of much larger particles also, the less perfect polarisation from which counterbalances the more perfect polarisation from the larger number of smaller ones. The distribution of size amongst the primary particles of Fig. 6 is therefore more heterogeneous than in Fig. 4. There were more particles dispersed and the mass was distributed between a number of comparatively large particles and a much larger number of comparatively small ones.

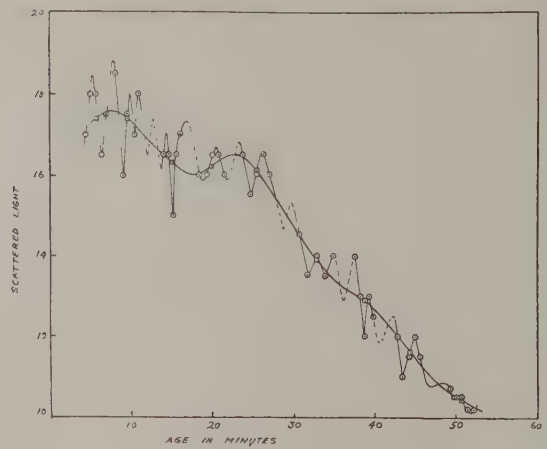

FIG. 5.—CADMIUM OXIDE.

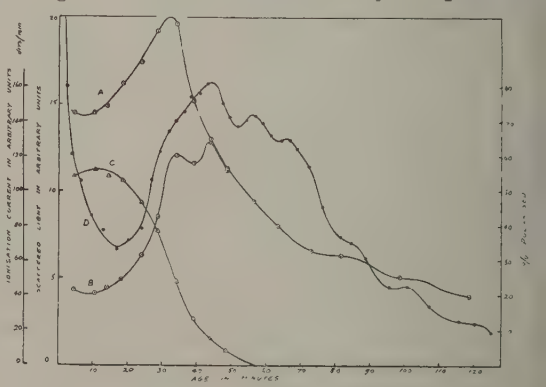

FIG. 6.—CADMIUM OXIDE.

This seems to account for the difference in behaviour. The small particles

tend to aggregate with the large ones rather than with one another, and this tendency increases as their number diminishes. This accounts for the rapid loss in the polarised light. The continuous growth of the large particles at the expense of the small increases their individual scattering power; so the total brightness increases until this effect is counterbalanced by the loss due to their aggregation and sedimentation.

The curves of Fig. 6 do not show well marked fluctuations, and these only appear after the maximum. The ionization curve shows rapid fluctuations before the maximum, and these continue subsequently. Prior to the maximum the dismembered particles do not greatly affect the scattering; which conforms with the view that disruption is the exact reverse process of aggregation, the primary particles remaining as distinct entities throughout the life of the cloud.

The initial distribution of mass amongst the primary particles in Fig. 6 is interesting, because the cloud, instead of being produced in dust-free air, was dispersed in the residues from a cadmium oxide cloud dispersed three days previously. The medium therefore contained such of the fine particles of the previous cloud as had not deposited in this period. Before dispersal the medium appeared optically empty. The electricity consumed by the arc (3·0 amps. $\times$ 40 secs.) was double that used in Fig. 6. (2·0 amps. $\times$ 30 secs.). In dust-free air this would have given normally a much brighter tyndall-beam. Actually the brightness was less and the colour more white. The minute particles left in the medium appear to have acted as nuclei for the condensation process, and collected most of the products vaporized by the arc. Had all the vapour deposited on these particles we should have obtained for these systems the analogue of Zsygmondy's[11] method of depositing gold on gold nuclei in colloidal solutions.

The effect feels more familiar when we remember that the best nuclei on which to grow large crystals from supersaturated solutions are tiny crystals of the same sort. The cloud particles are cadmium oxide crystals.[12]

Experimental.—II.

As the weight concentrations of clouds produced from an arc were unknown observations were made on clouds dispersed by volatilizing known masses of arsenic trioxide from a porcelain boat. The boat was placed on bare nichrome wire, and the contents volatilized by heating the wire by a constant current left on for the arbitrary period of four minutes (timed $-$ 2·0 mins. to $+$2·0 mins.) in each experiment. During the process a draught was maintained across the boat by means of a fan, and to ensure constancy of conditions the dispositions of the fan and the boat were never altered. The fan was kept running continuously throughout each experiment to maintain homogeneity in the cloud, although this probably accelerated the rate at which it disappeared.[4]

A "Pointolite" lamp placed outside one end of the chamber was used as a source of light. The beam, collimated and cut down to a cross-section of one sq. cm. by diaphragms, passed inside a steel tube parallel to the face of the cistern. The inner end of the tube was closed by plate glass, through which the incident beam passed into the cloud. The beam was ultimately absorbed by passing into a second cylinder whose inner surface was blackened. The tyndall-light was viewed just after entering the cloud through a hole cut in the front of the chamber. It was

hoped that in this way the intensity of illumination at the point of observation would be independent of the density of the cloud.

The clouds were dispersed in dry air free from dust and carbon dioxide. In general, the scattered light was partially plane polarised and slightly green in colour. Fig. 7 shows the results obtained from the dispersal of 45 milligrams of As_2O_3 in the 850 litre cistern. *A* gives the total scattering, the sum of the components. *B* is the polarised light -the ratio of the difference between the components, to their sum expressed as a percentage, and *C* is the ionization current in arbitrary units. The same general changes occur here as with arc clouds, so need not be discussed. As *B* depends upon the difference of two quantities, both of which ultimately become small and difficult to measure, its accuracy diminishes as the cloud ages. Within the limits of accuracy of the measurements the fluctuations in *A*, *B* and *C* are practically synchronous.

Observations were taken on a series of clouds in which the masses of arsenic trioxide dispersed varied from 15 mg. to 500 mg. The ionization currents were always weak. With a constant field on the ionization chamber, the initial currents did not vary greatly throughout the series. The currents were always oscillatory, and on the whole diminished fairly steadily as the cloud aged. The reciprocal of the current strength plotted against age gave a curve convex to the axis of time in all cases. The initial number of positive charges was therefore unequal to the initial number of negative charges. A direct test showed that there were more positive charges than negative. As the process of vaporization is unlikely to produce electrification, it appears probable that the initial charges arise from a low temperature emission from the heated nichrome wire. This would account for the excess of positive charges and the lack of variation with the mass of material dispersed. A blank experiment with no material in the boat showed that the heater did actually emit ions.

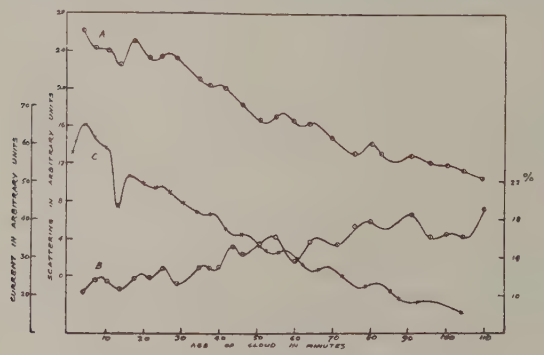

FIG. 7.—ARSENIOUS OXIDE.

CONCENTRATION AND TYNDALLMETER READINGS.

In each cloud of the series the intensity rapidly increased to a maximum, which occurred close to the arbitrary zero of time. Where sufficient observations were obtained, the readings before the maximum fell on straight lines, which cut the time axis approximately one minute after making contact in the heating circuit. This seems to indicate that the arrangements for producing dispersal worked fairly consistently throughout the series. With increasing mass dispersed the maximum brightness of the tyndall-beam increased, and in general the percentage of polarised light present decreased. When 400 mg. and 500 mg. were dispersed, there was no

appreciable difference between the values of the two components. Fig. 8 shows the variation of intensity with the mass dispersed. If logarithms of the mass dispersed are plotted against logarithms of the maximum brightness, the points lie about a straight line of slope 2/3. Hence the brightness of the tyndall-beam is given closely by the equation

$$I = A \cdot m^{2/3}$$

where A is a constant; m the mass of material dispersed. This is the equation to the smooth curve. The clouds behave, therefore, as if they contain a constant number of particles which reflect light from their surfaces. Under these conditions the masses of the individual particles in different clouds become proportional to the mass dispersed and their surfaces to the quantity $m^{2/3}$. The growth in size of the primary particles with increasing weight concentration is consistent with the general decrease in the polarisation shown as the mass dispersed increased.

It has already been mentioned that the nichrome wire heater emits ions during the dispersal of the cloud. It also emits nuclei (particles), as can be demonstrated by passing the air from its neighbourhood into a Wilson expansion apparatus, where they are caught with a very small expansion. If we may assume that their number remains as constant in each experiment as the number of ions emitted, the above results become explicable if condensation takes place upon them, for many must be produced before the boat is hot enough to vaporize its contents. From a super-saturated solution crystal growth occurs less readily spontaneously than upon foreign nuclei.

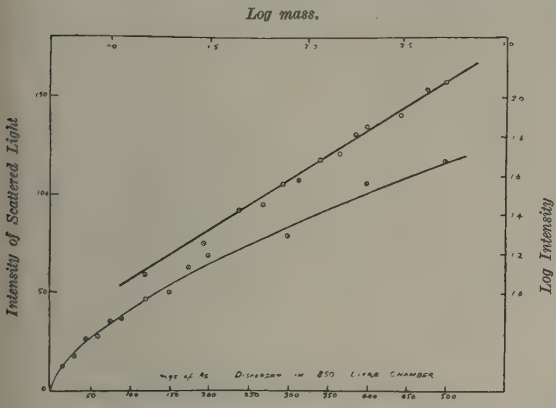

FIG. 8.—ARSENIOUS OXIDE.

The other limiting case in which the number of condensation centres increases proportionally with the mass dispersed seems to have been discovered by Tolman[13] with ammonium chloride smokes. Here the average *size* of the particles apparently remained constant, and the brightness of the tyndall-beam was directly proportional to the concentration. Unless special precautions are taken, it is to be expected that usually both the number and size of the particles will increase with increasing mass dispersed. Even when the *same* mass of material was dispersed it was found with our arrangements that the maximum brightness and the percentage polarised were never *exactly* the same, which is perhaps not unnatural.

THE FLUCTUATIONS IN BRIGHTNESS.

The stronger components for clouds of various concentrations are shown in Fig. 9. The curves are plotted from the "mean" values, and are drawn to include each observation. As drawn, several of the fluctuations show a rough tendency to synchronise, which would have appeared more marked by allowing some of the

points to fall off the curves. If the curves prove similar when measured under more ideal conditions, the time of occurrence of a given fluctuation would be independent of the mass of material dispersed and of the total surface area of the particles, since their number is the same in each cloud. This suggests that the fluctuations arise from some effect of the gaseous medium on the particles, and that they appear after the surfaces of the particles have suffered a definite number of molecular impacts.

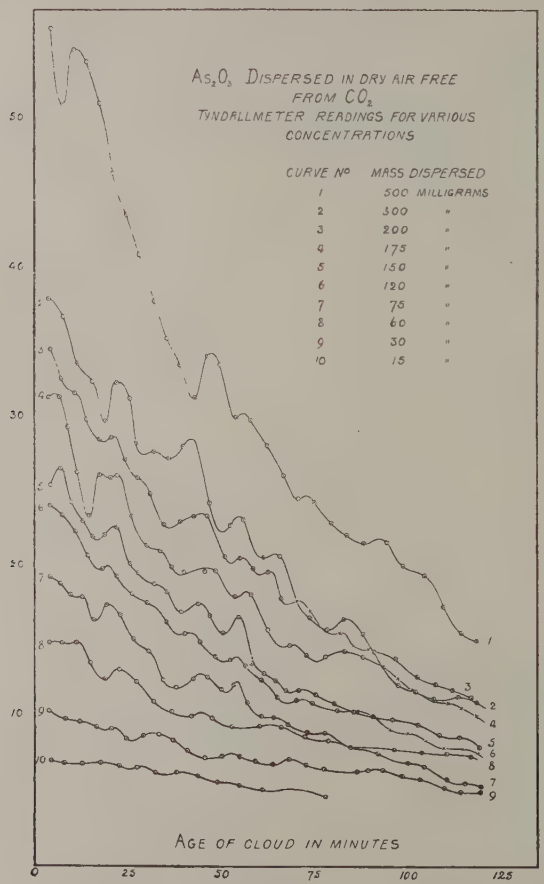

FIG. 9.

On this view, the departures from synchronism in Fig. 9 would be attributed partly to the method of reducing the readings and partly to variations in temperature and pressure. Each cloud of Fig. 9 was dispersed on a different day, and, owing to the bulky nature of the apparatus, had to be measured at the temperature and pressure of the day.

As in the case of clouds produced from the arc, the actual fluctuations in brightness occur much more rapidly than is shown by the curves of Fig. 9. In Fig. 10 an attempt has been made to record the individual observations for the two components. The cloud is the same as that of Fig. 7. The observed points are joined by straight lines. The diagram gives a more accurate picture of the rapidity of the fluctuations, and illustrates very well the extremely complex systems with which we are dealing. The percentage curve which indicates changes in the degree of dispersion is calculated from the components as drawn. Although it may not record all the variations which occurred, an attempt has been made to analyse it. The origin of time is taken as one minute after making contact in the heating circuit. It is found that the times of occurrence of a large number of the minima are given by the formula

$$t = Ar^n$$

where n is an integer and A and r are constants. A comparison of the observed

times and those calculated from the formula with $A=3{\cdot}664$ and $r=1{\cdot}097$ is given in the Table. The deviations of the calculated values from the observed are well within the limits of experimental error.

TABLE.—*Comparison of Observed Times of Occurrence of Minima with the Times Calculated from the Formula* $t=Ar^n$.

n	Calculated times.	Observed times.	n	Calculated times.	Observed times.
1	4′ 01″	...	19	21′ 27″	21′ 30″
2	4′ 25″	4′ 30″	20	23′ 33″	23′ 30″
3	4′ 50″	...	21	25′ 50″	25′ 30″
4	5′ 12″	...	22	28′ 22″	28′ 30″
5	5′ 50″	6′ 00″	23	31′ 07″	31′ 00″
6	6′ 24″	...	24	34′ 10″	34′ 00″
7	7′ 01″	7′ 00″	25	37′ 30″	37′ 15″
8	7′ 42″	...	26	41′ 08″	40′ 45″
9	8′ 28″	8′ 30″	27	45′ 09″	44′ 36″
10	9′ 18″	...	28	49′ 33″	49′ 30″
11	10′ 12″	10′ 15″	29	54′ 23″	54′ 30″
12	11′ 12″	...	30	59′ 41″	59′ 45″
13	12′ 16″	12′ 00″	31	65′ 30″	65′ 30″
14	13′ 29″	13′ 30″	32	71′ 54″	72′ 00″
15	14′ 47″	14′ 36″	33	78′ 55″	...
16	16′ 14″	...	34	86′ 36″	86′ 36″
17	17′ 48″	17′ 15″	35	95′ 02″	95′ 15″
18	19′ 32″	20′ 00″	36	104′ 18″	105′ 30″

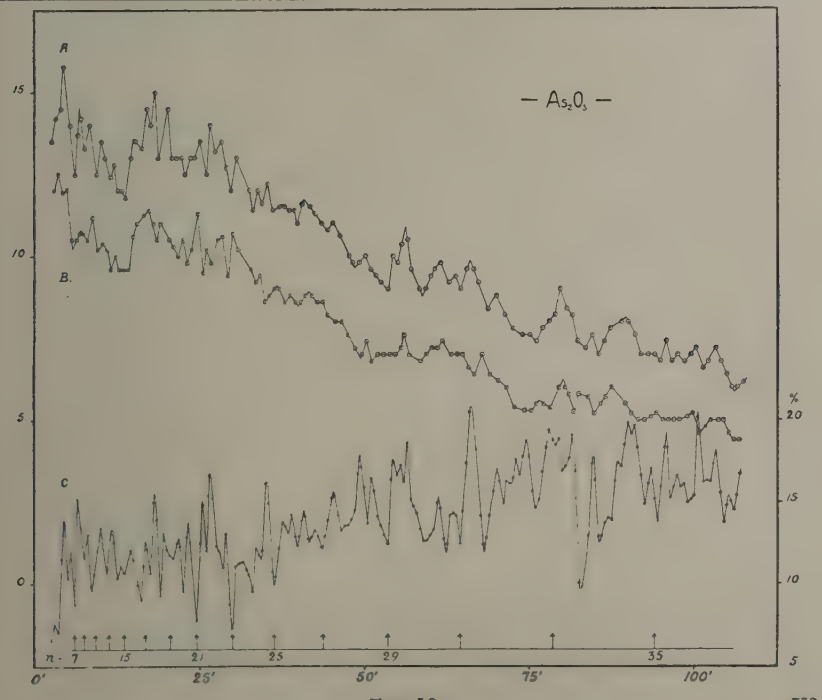

FIG. 10.

The calculated times for some odd values of n are shown by arrows in the figure. These seem to divide the fluctuations into groups, as if the phenomena involved were periodic. As the cloud ages the time required to describe a group of fluctuations lengthens exponentially. A similar relation was found to hold for the rapid fluctuations with cadmium oxide. The investigations along these lines were not carried far, for it is obvious that for further progress mechanical registration of the fluctuations is necessary.

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XXXVI.—NOTE ON THE TRANSMISSION OF CATHODE RAYS THROUGH THIN FILMS.

By B. L. Worsnop, *B.Sc., Ph.D.*, University of London, King's College.

Received June 12, 1928.

Abstract.

The results of the experiments of G. P. Thomson on the transmission of electrons through thin films are discussed. It is suggested that the explanation in terms of the Debye-Scherrer diffraction is untenable in certain cases. In particular for the case of celluloid films, and " amorphous " films generally, it is suggested that scattering ofm the echanical waves at centres might account for the observed results.

Calculation shows that the distance apart of the scattering centres is of the order of the distance between atoms. An analogy between this case and that of X-rays (Keesom and Smedt) is made, and it is shown that the test between a scattering and a diffraction origin of the rings is the relative diameters of the rings.

A brief announcement of another " diffraction " experiment is made.

RECENT theoretical discussions on the new quantum theory have shown an analogy between electrons and waves of high frequency, the frequency ν being given by $\nu=mc^2/h$. This has led to experiments designed to show that electrons behave as if they were waves. Evidence of this kind is to be found in the scattering of electrons in gases (Dymond*), by crystal faces (Davisson and Germer† and Davisson and Kunsman‡), and more recently in the experiments of G. P. Thomson.§

In the experiments of Thomson a narrow pencil of electrons was directed normally on to a very thin film, and the result examined on a photograhic plate, as in the corresponding case of the production of patterns by the Debye-Scherrer powder method in X-rays. In these experiments it was found that, in addition to the direct transmitted beam, rings were present on the plate when thin films of aluminium, gold, celluloid and an unknown substance were used. To account for these results the view was taken that the electron had a definite wavelength, given by $\lambda=h/mv$, and that the mechanical waves were diffracted in some way in the films.

In a discussion on the results it is stated that if the rings are of the nature of a diffraction pattern, the diameter should be proportional to the wavelength, or that D/λ=a constant, where D is the diameter of the ring.

When v is small we may write $\lambda=h/m_0v$, where m_0 is the rest mass of the electron ; also $\frac{1}{2}mv^2=Pe/300$, where P is the applied potential measured in volts—i.e., $\lambda=(h/m)\{150/(Pe/m_0)\}^{\frac{1}{2}}$, so that for this approximation we have $D/\lambda=DP^{\frac{1}{2}}(m/h)(e/150m_0)^{\frac{1}{2}}$=a constant. This means that if the applied potential be varied to produce a variation in λ, then $D\sqrt{P}$ should be constant to be consistent with a diffraction origin of the rings. This constancy was found to exist approximately in the

* Nature, **118**, 336-7 (1926).

† Phys. Rev., **30**, 705 (1927).

‡ Science, **64**, 522 (1921). Phys. Rev., **22**, 242 (1923).

§ Proc. Roy. Soc., Vol. 117, p. 600 (1927).

cases tested, and better agreement was found when correction was made for the mass of the electron in terms of its velocity. The tabulated values which agree to within 4 per cent., including the correction factor, were for $D\sqrt{P}(1+Pe/1200\ m_0c^2)$, instead of $D\sqrt{P}$.

In the case of the metal films, it was suggested that the rings were produced in the same way as the "rings" of the Debye-Scherrer powder method in X-rays. By suitable selection of atom layers, Thomson was able to calculate the lattice constants of the minute crystals involved, and the result of the calculation came to be within about $6\frac{1}{2}$ per cent. of the accepted values obtained by X-ray methods.

It is not so easy to see, however, how such effects may be used to explain the production of the rings in the case of celluloid. As far as one can gather, the cause in this case was attributed to diffraction at minute centres in the film, as in the production of haloes.

Now it appeared to the writer that the observed rings are very similar in appearance to the concentric rings which were found in the scattering experiments of Keesom and Smedt.* These observers investigated the scattering of a very narrow pencil of X-rays in liquid oxygen and nitrogen, also in water and carbon bi-sulphide. They used a method very similar to that of Thomson, but the incident beam was the filtered radiation from a copper target X-ray tube. For these liquids it is clear that no explanation in terms of a random crystal distribution meets the case, and the authors were led to explain their results in terms of a theoretical investigation of Debye and Ehrenfest. This theoretical investigation deals with the problem of the scattering of radiation by two centres separated by a distance s, the line joining the centres inclined at all possible directions to the incident radiation. A deduction of the result for the case of two electrons is to be found in Compton's "X-rays and Electrons," Appendix IV, page 384. It is shown from considerations of scattering on classical principles that the intensity of the scattered beam in any direction φ is given by the expression

$$I_\varphi=\frac{Ie^4(1+\cos^2\varphi)}{r^2m^2c^4}\left\{1+\frac{\sin x}{x}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $x=(4\pi s/\lambda)\ .\ \sin(\varphi/2)$, and I is the incident intensity and λ is the wavelength of the incident radiation—i.e.,

$$I_\varphi=2I_e(1+\sin x/x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where I_e is the scattering by one electron.

This leads to the result that, in a direction inclined to the incident beam, the scattered beam shows fluctuations of intensity, the directions of the maxima and minima being governed by the values of $\sin x/x$. It is therefore clear that maxima occur when x is approximately equal to $5/2\pi$, $9/2\pi$, $13/2\pi$, etc., or more precisely when x is $2{\cdot}459\pi$, $4{\cdot}477\pi$, $6{\cdot}484\pi$, etc.

In the X-ray case referred to the angle φ_m corresponding to the first maximum was deduced from the diameter of the ring, and substitution was made in the formula $x=(4\pi s/\lambda)\sin(\varphi/2)$ of the value $x=2{\cdot}459\pi=7{\cdot}72$; $\varphi_m=D/2L$

or

$$s=7{\cdot}72\lambda/4\pi\ .\ \sin(\varphi_m/2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Journal de Physique, p. 144 (1923).

The calculated values of s for the liquids used in the experiments came out of the order of 4 to 6 Å.U. Also the distance between the molecules of these liquids when calculated from the expression $d=1{\cdot}33\sqrt[3]{M/\varrho}$—i.e., assuming close packing of the molecules, was found to be in very good agreement with the corresponding value of s. This suggested that the scattering in these cases was from molecules, which are presumably close packed in the liquid, presenting a regularly spaced system of scattering centres. More evidence of the rings of maximum intensity is available, for X-ray scattering. For example, Hewlett* used an ionisation method to investigate the scattering from mesityline, using X-rays of wavelength 0·7 Å.U. He found a maximum at about 10°. Using equation (2), this gives the value of s about 5 Å.U. It seems therefore that the expression is one which is at any rate approximately true, and that it may be applied to the case of scattering from a large number of scattering centres.

It would appear that something on these lines might be used with advantage to explain the rings produced with celluloid, and it also seems desirable to see how far this point of view meets the case of the metal films in the Thomson experiments.

If we substitute for λ the value $\lambda=(h/m_0)\{150/P(e/m)\}^{\frac{1}{2}}$ in the expression (2) above, we have

$$s=\{7{\cdot}72h\sqrt{150}/4\pi m\sin(\tfrac{1}{2}\varphi)\}\div\sqrt{P(e/m)}=\text{constant}/D\sqrt{P}\quad .\quad .\quad .\quad .\quad (3)$$

and we see that s=a constant$/D\sqrt{P}$. In other words, the constancy of $D\sqrt{P}$ is demanded if we assume *scattering* of the mechanical waves associated with the electron, as distinct from diffraction.

This point of view seems a reasonable one, as analogy between X-rays and mechanical waves holds in the case of "reflection" at the face of crystals. The presumption is that other X-ray properties should be shown in the waves, and in particular that of scattering.

Unfortunately, the data for celluloid is not so complete as for the metal films, and therefore use is made of the data for aluminium and gold as an alternative to the treatment given by Thomson. If we make allowance for the correcting factor for the mass, and use the mean corrected value of $D\sqrt{P}$ as obtained for aluminium (434), we find on substitution

$$s=h\times7{\cdot}72\sqrt{150}/m_0 4\pi\sin(\varphi/2)\sqrt{P(e/m)}=2{\cdot}22\ \text{Å.U.}$$

Making similar substitution for gold, we obtain $s=2{\cdot}39$ Å.U. If we further follow Keesom and Smedt, and evaluate $d=1{\cdot}33\,.\,\sqrt[3]{M/\varrho}$, we find in the two cases $d=3{\cdot}61$ for aluminium and $d=3{\cdot}63$ for gold.

This treatment, therefore, gives the right order for the distance between the scattering centres, but the difference between s and d suggests that this is not a case of scattering by molecules. It is interesting to note that the accepted values of the distance between the atoms in molecules of fluorides of aluminium, gold, etc., as calculated from band spectra data is of the order of 1·7 to 2·3 Å.U. This naturally suggests that the scattering centres might well be the *atoms* in the films. The diameters of the rings on this assumption should be in the ratio :—1 : 1·82 : 2·63, etc. According to the theory of "reflection" at minute crystals with a random

* Hewlett, Phys. Rev., 20, 688 (1922).

distribution, and taking the different faces, more rings should appear, and, as stated at the outset, Thomson finds these, and obtains an agreement to within 7 per cent. of the known spacings. It seems therefore that for such films the effect corresponds to a Debye-Sherrer picture, giving another analogy with X-rays. For substances like celluloid this process does not seem so likely, and it has been suggested for this case that the effect may again be due to diffraction at centres, as in the production of haloes.

It is here suggested that in a case like this the rings may be due to scattering; the test between these two causes is to be had in the measurement of the intensities and the diameters of the rings. For diffraction the diameters are in the ratio 1 : 1·6 ; 2·3 : 3 for scattering the diameters are as stated above, viz., 1 : 1·82 : 2·63, and any regular arrangement of scattering centres should produce this result if we may make this additional analogy with X-rays.

To test this it seems desirable to have data on the transmission of electrons through some "amorphous" substance of known composition, and I understand that results of this type will shortly be available. It is of interest to note that in the case of rings with celluloid Thomson says that the diameters of the first and second rings are approximately as 1 : 2.

At the present an experiment is being carried out in which many of the consequences of the wave nature of electrons are under independent test. In brief, these experiments consist in sending a beam of electrons at a known angle on to a ruled diffraction grating in much the same way as has been done in the case of X-rays. It is hoped to make a preliminary announcement of the results of these experiments quite soon. Incidentally, it may be possible to test the conclusions given above by means of the apparatus.

In conclusion, I wish to take this opportunity to thank my colleague Dr. H. T. Flint for many helpful discussions and advice on this subject, and also to thank Prof. E. V. Appleton for the interest he has taken in discussing the problem which forms the subject of this note.

XXXVII.—BASIC MEASUREMENTS OF THE EFFECTIVE RESISTANCE OF CONDENSERS AT RADIO FREQUENCIES.

By D. W. Dye, *D.Sc.*, *F.R.S.*, the National Physical Laboratory.

Received June 22, 1928.

Abstract.

Following a very brief introductory statement concerning losses in condensers at radio frequencies, a description is given of a special air condenser so constructed that a change in its capacity may be made without change in the losses. The method of using such a condenser to measure the losses in a variable air condenser is next described. Measurements made by means of the special condenser on the losses in a high-class standard variable air condenser are given, and it is shown that the losses at any reading and any frequency may be represented to a good approximation by a fixed resistance plus an effective resistance represented by a constant power factor in the insulating material and hence proportional to the reciprocal of the square of the capacity; a third component of the effective resistance is proportional to the reciprocal of the square of capacity and to the square of frequency and is analogous to that which would be given by a constant shunt resistance.

The paper concludes with an appendix giving calculations of the effective resistance of the conductors of the special condenser whence it is shown that this may be neglected.

THE establishment of a basis for the measurement of the losses in condensers at radio frequencies is not an easy matter when certainty greater than that represented by the assumption that a high class air condenser has zero loss is desired.

The accumulated measurements of effective resistance in all its aspects at radio frequencies has led to the opinion that the losses in even very good variable air condensers is not of negligible importance.

A knowledge of the losses in condensers is therefore of considerable importance, not only for its own sake, but also in relation to the whole question of effective resistance measurements on inductive coils, etc., whenever a method is used other than one which measures directly the energy dissipated in any apparatus.

There are two classes of measurement which in the past have pointed to the conclusion that uncertainties in the knowledge of the losses of the condensers used may have been the cause of the discrepancies found.

Thus, thermal methods of measuring effective resistance of inductive coils have been compared with measurements made by methods involving the whole of a resonant circuit containing a good variable air condenser. In such cases when all care has been used a residual difference has been found indicating that a small loss resides in the condenser.

Again, in the cases where inductive coils of design such that the losses can be theoretically calculated have been constructed and carefully measured, the results, when a thermal method has been used have tended to be smaller than when a circuit method was adopted. The accumulated errors associated with the chain of measurements and calculations of which the final link is a good condenser are, in the present state of the art, such that the differences ascribed to the condenser can hardly be considered a measurement of its losses, except in cases where such losses are several times that which a really high class condenser may have.

In spite of the present unsatisfactory accuracy judged from the standpoint of

the condenser, there would seem to be hope that further carefully made measurements, using coils of calculable resistance which can be measured by thermal and other methods, would enable the losses in a good air condenser to be measured to an accuracy of 20 per cent. or 30 per cent.

The problem of condenser loss measurement has been directly attacked by a few experimenters, and a very short résumé of these may be permitted here for the sake of completeness.

In 1926 Callis* published an account of measurements of losses in condensers made by an ingenious method in which two nearly identical coils were used.

The principle is as follows: Resonance is established in an oscillatory circuit, including one of the coils and the variable air condenser under measurement. The effective resistance of the whole circuit is measured by a usual method. A second similar measurement is made using the other coil.

A third measurement is now made using both coils in series in the circuit located, so that their mutual inductance causes the total effective inductance to be the same as before. Resonance is maintained without change in the capacity, but the effective resistance of the circuit has been increased by that of the second coil only. The difference between the measured total resistances of the circuit in the two cases, therefore, gives a measure of the effective resistance of the second coil, involving no assumptions regarding the condenser losses. The latter are thereby determined by difference from one of the first two measurements.

The general consistency of the results obtained justify the method to the somewhat limited accuracy attained and desired in the type of condenser measured. One fact has, however, been lost sight of in the method. The total effective resistance of the circuit in the second case will have a part due to what may be called the mutual resistance of the coils. Since each coil is present in the magnetic field of the other additional eddy current losses will occur from this cause. In the actual coils used by Callis the wire was thin, so that their effective resistances were but little greater than their direct current resistances; the mutual resistance was therefore small also. On the other hand, the total resistance of the circuit was thereby so large relatively that only in the case of condensers with considerable losses could reliable measurements be made. The corrections on account of self capacities of the coils are also of importance.

It is possible that a good case could be obtained using coils of much lower resistance and then making definite measurements of the mutual resistance by observing the increase in resistance of the circuit when the second coil is brought into position but not connected up.

This difference should be one-half that which will exist when both coils, assumed similar, are included in the circuit. Further measurements along these lines would be worth making.

The direct attack on the condenser has also been made by two methods; one is a thermal method, and the other involves the use of a specially designed condenser. There seems little doubt that a solution of the problem of condenser losses can be met by the design and proper use of special condensers.

The difficulties of the thermal method will be seen from a consideration of the

* C. D. Callis, Measurement of the Resistance of a Condenser at Radio Frequencies, Phil. Mag., Vol. 1, 7th ser., p. 428 (1926).

quantities involved in a typical case. A high class condenser of 500 $\mu\mu$F capacity might have a resistance of 0·03 ohm at a frequency of 10^6 cycles per second. Taking a root mean square applied voltage of 500 as the safe maximum, the current would be about 1·5 ampere and the losses about 0·07 watt. The condenser will, of necessity, have a considerable thermal capacity, causing very slow changes in temperature. Specially made mica condensers, by reason of their small volume and low thermal capacity, might however yield accurate results by a thermal method; such experiments would be worth trying.

A method recently described in an important Paper by E. Offerman* makes use of a specially designed condenser, consisting of three plates A, B and C, so disposed that A and B have a pure capacity to one another, and are each supported on C, with insulating material between. Three capacities are thus formed, C_2 and C_3, each with losses due to the solid insulators, and C_1, which is considered perfect. The design is such that the three capacities are nearly equal.

The principle of the measurements is to observe the differences in losses of the two-terminal condensers formed by shorting each of the capacities in turn. Thus, when C_3 is shorted, C_1+C_2 has a loss due to C_2 equal to, say, R_2. C_1+C_3 has a loss R_3, and C_2+C_3 has a loss R_2+R_3. Hence, R_2 and R_3 are determined. The work carried out by the authors of this method, including numerous measurements on various types of condensers, together with the apparently highly sensitive means used in the actual measurements, indicate that the method is of considerable value.

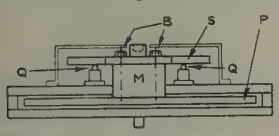


FIG. 1.—CONSTRUCTION OF CONDENSER.

The chief source of uncertainty lies in the unwieldy shape of the condenser, which was not screened. A modified design could doubtless be constructed to remedy this defect and enable measurements on really good condensers to be made. The results obtained indicate an uncertainty in power factor measurement of 2×10^{-5} corresponding to 0·006 ohm in a condenser of 500$\mu\mu$F at 10^6 cycles per second.

The necessity for the use of specially constructed condensers arises on account of the conductor losses in any normal type of variable condenser, otherwise, as will be shown later, it is quite valid to assume that the losses in a variable air condenser, with moderately large air gaps, are independent of the angular setting. On such an assumption there are no real difficulties in measuring the losses in another condenser if the standard is left connected to the circuit all the time.

The feature of the condenser about to be described is that the conductor losses within it may be considered quite negligible, and that a change in its capacity can be made without any change whatever occurring in the losses at constant voltage.

DESCRIPTION OF THE CONDENSER.

The design is very simple, as shown in Fig. 1. It consists of a thick brass plate P hung by means of a three-armed spider S upon three quartz rods Q, and located centrally between two other brass plates. The location is by hole, slot and plane. The attachment of the plate P is by means of the very thick central copper block M,

* E. Offerman, Valve Method of Measurement of Losses in Condensers at High Frequencies, Zeit. für Hochfreqy., Vol. 26, p. 152 (1925).

which contains a mercury cup at the top. Three plates P of different diameters are provided, so that three different capacities may be obtained. The attachment of the plate P to the copper block is by means of three bolts B. When these are undone and removed the plate P rests upon the lower of the two outer plates, and the residual capacity of the spider and block to the enclosure containing it is the only capacity of the condenser. This capacity is about $18\mu\mu$F. It is now necessary to discuss the correct method to use such a condenser in order to obtain accurate measurements of the effective resistance of another variable air condenser by the method of substitution.

The assumption made is that the standard condenser consists of a small fixed capacity with constant losses at a given frequency, and that a large fixed capacity can be added without causing any increase in the losses.

In considering the arrangements of the circuits for measuring the unknown condenser, it is convenient to represent the circuit as in Fig. 2.

The standard condenser is shown at K, with the capacity of the spider, etc., shown as K_1 shunted by S. The leads from the points of division a, b to this condenser are considered to have an indeterminable resistance r_k, and this branch carries current I_k. The right-hand branch contains the unknown condenser C, with equivalent series resistance R. An additional small condenser C_1, with shunt resistance T, is connected as shown in order to balance K_1 as far as capacity is concerned. This branch carries current I_c. The total current I is measured by thermo-junction and heater, and in the main circuit resistance can be added as usual for the purpose of resistance measurement by the ordinary resistance variation method. The coil L completes the circuit. It is assumed that a quantity R can be measured, which is the difference in the effective resistance of the whole circuit, referred to the current through the thermo-junction and heater, when C replaces K. If we consider the losses in the circuit between the points a, b for the two cases we have :

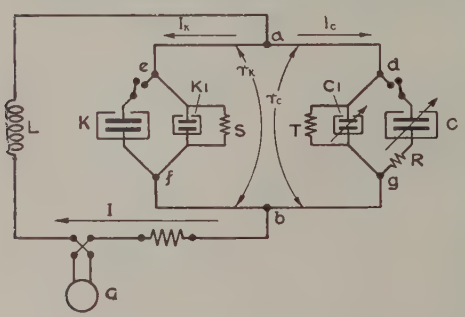


FIG. 2.—SCHEME OF EFFECTIVE IMPEDANCES IN COMPARISON OF CAPACITIES.

(1) Test condenser C in circuit and K disconnected.

$$\text{Losses}=I_k^2r_k+E^2/S+I_c^2r_c+E^2/T+I_c^2RC^2/(C+C_1)^2$$

(2) Standard condenser K in circuit and C disconnected.

$$\text{Losses}=J_k^2r_k+E^2/S+J_c^2r_c+E^2/T.$$

On the assumption that $C=K$ and $C_1=K_1$ we have

$$I_k=IK_1/C_t;\quad I_c=I(C+C_1)/C_t$$

$$J_k=I(K+K_1)/C_t;\quad J_c=IC_1/C_t$$

where $C_t=C+C_1+K_1$ and $I=I_c+I_k=J_c+J_k$

On substitution it will be found that

$$\Delta R = 1/C_t^2 \times [(C^2+2CK_1)r_c - (K^2+2KK_1)r_k + C^2R]$$
$$= (C^2+2CK_1)r_c - (K^2+2KK_1)r_k + C^2R/C_t^2.$$

If $r_c = r_k$ this reduces to

$$\Delta R = RC^2/C_t^2$$

whence

$$R = \Delta R C_t^2/C^2$$

It will be seen therefore that, in order for the substitution method to give results not involving leads, it is necessary for C_1 to be made equal to K_1 and r_k to equal r_c.

Experimental Procedure.

The condenser described was set up in a circuit as in Fig. 2 for the purpose of measuring the effective resistance of one of the best standard variable air condensers of the laboratory.

In order to satisfy the conditions outlined above, the leads *ad*, *ae* were very thick copper rods with one bent end of each dipping into mercury cups in a copper block at "*a*." They were equal in length, and that rod going to *K* had its bent end directly dipping into the mercury cup on the spider supporting the plate *P* of *K*. In a similar manner the leads *bg* and *bf* were equal thick copper rods connected to the screens of the respective condensers.

The small capacity C_1 made equal to K_1 was a small screened variable air condenser permanently connected across the ends *d*, *g*.

Experiments were made using each of the three plates *P* in turn, so that measurements were made at three different settings of the condenser under test. The measurements were made at a number of frequencies in each case.

Various methods of observation were tried, and much difficulty was experienced in attaining the accuracy desired on account of the small proportion of the resistance difference sought compared with the total resistance of the circuit.

The method finally adopted was that of simple resistance variation specially adapted and carried out to ensure the utmost possible accuracy in the measurement of the resistance difference resulting from the substitution of one condenser for the other.

Owing to unavoidable small differences in induced electromotive force when one condenser is substituted for the other in measurements of this kind, it is not sound simply to adjust a low range variable resistance to give equality of deflection of the current-indicating instrument upon changing one condenser for the other.

It is essential to measure the resistance of the circuit each time. By the use of an auxiliary small resistance, however, and by a proper procedure in observing, it is possible to throw the primary responsibility upon direct observation of a small difference of deflection, and not upon the ratio of two considerably different deflections.

The current measurements were made using a vacuum thermo-heater and galvanometer. The galvanometer scale was at about 5 metres distance, and readings could be taken to an accuracy of 0·2 mm. on a scale 2 metres long. The readings were taken on a time basis as from the instant of closing the galvanometer circuit, so as to eliminate the effects of zero drift of the galvanometer spot. The procedure

was as follows: the standard condenser was first connected in circuit at "*e*" with no added resistance, resonance was carefully obtained, the deflection being adjusted to a value θ_0, not very different from a reading of 1000 on the equally divided scale. A suitable resistance was chosen and inserted so as to bring the deflection down to approximately 500 on the scale $=\theta_1$. The galvanometer was got into a cyclic state by inserting and shorting the added resistance alternately into and out of the circuit a number of times.

Alternate readings of θ_0 and θ_1 were then taken, and the deduced value of θ_1, corresponding to a standard value of $\theta_0=1000$, was determined.

The same procedure was repeated after interchange of the condensers, performed by unbolting the plate *P* and connecting the insulated terminal of the test condenser *C* to the end "*d*" of the thick copper rod "*ad*."

A second deflection, θ_2, corresponding to the same standard value of θ_0, was obtained. The quantity $\theta_2-\theta_1$ was very small, and of course represents the whole of the difference sought. The experiment was therefore repeated a considerable number of times, sandwiching the series for one condenser between that for the other.

From the simple and well-known equations the quantity ΔR, referred to the circuit at the point where *I* is measured, may be deduced from the observations directly, by means of the derived equation

$$\Delta R=\Delta\theta/2\times\text{added } R\times\sqrt{\theta_0/\theta_1}\times 1/(\sqrt{\theta_0}-\sqrt{\theta_1})^2$$

for the case concerned, in which θ_1 and θ_2 are nearly equal and are measured on a uniformly divided scale.

The values of ΔR so obtained were then converted into their equivalent values expressed as the effective resistance of the condenser itself, using equation (1). In general, C_t was not very much greater than *C*, except for the case of the smallest of the plates *P* of the standard condenser.

The three plates used gave capacities of approximately 500, 300 and 180 $\mu\mu$F respectively.

The measurements on the variable condenser under test were therefore made at readings corresponding to these values.

Each value of the variable condenser was measured over the range of radio frequencies comprised between the limits of about 1500 and 50 kilocycles per second.

The results when plotted on evenly divided scales of "series resistance" and the reciprocal of frequency respectively gave lines which were curved slightly in the direction indicating a rate of increase in *R* greater than the rate of increase of $1/n$, such as would be caused by a combination of a loss represented by a constant power factor in the insulation material of the condenser, together with that represented by a constant shunt resistance.

When plotted in terms of the reciprocal of C^2, however, straight lines are obtained of which the intercept on the resistance axis gives the series resistance; and the slope is nearly but definitely not quite proportional to $1/n$.*

The three lines corresponding to the three capacities tested converged to values of *R* very near to one another. The actual value was very small, being about 0·007 ohm.

* In ordinary condensers the losses are such that, on the scales used, the intercept on the resistance axis is very nearly zero.

It is of interest to see whether the values of effective resistance obtained are consistent with the assumption that the losses in a variable condenser can be considered as made up of those represented by

(1) A constant series resistance,

(2) A constant power factor in the insulation,

(3) A constant shunt resistance.

It must be clearly understood that the experimental results by no means prove this, but only that they are not very inconsistent with this assumption.

The effective series resistance of the condenser at any capacity and at any frequency would, on the above assumption, be equal to

$$R_a + \varphi C'/C^2\omega + 1/SC^2\omega^2$$

where R_a is the constant series (conductor) resistance,

φ is the power factor of the insulation,

C' is the capacity contributed by the insulation,

and S is the effective constant shunt resistance.

A suitable value to assume for $\varphi C'$ in order to fit the curves is $7{\cdot}5 \times 10^{-15}$; this, on the assumption that C' is of the order $20\mu\mu$F, would represent a power factor in the quartz insulation itself of about 4×10^{-4}, a not unreasonable amount.

The value of S in order to fit the change proportional to the square of the frequency is about $2{\cdot}5 \times 10^9$ ohms.

This value gives for the third constituent of effective series resistance the quantity $4 \times 10^{-10}/C^2\omega^2$.

The expression for the effective series resistance of the condenser at any capacity and any frequency becomes

$$R = 0{\cdot}007 + 7{\cdot}5 \times 10^{-15}/C^2\omega + 4 \times 10^{-10}/C^2\omega^2$$

Three curves have been calculated from this expression for the three capacities of 494, 314 and 184 $\mu\mu$F respectively corresponding to the actual capacities measured.

They have been calculated and plotted over the range of frequencies experimentally explored.

These curves, together with the experimental points, are shown in Fig. 3. Owing to the large range of resistance and frequency covered, the curves have been drawn to logarithmic scales.

It will be seen that fair agreement is obtained except at the highest frequency used on the two smaller capacities.

Later measurements carried out by a very sensitive bridge arrangement not yet published have shown that the results represented by the curves represent the losses to a very close approximation.

In view of the smallness of the power factor of the condenser, the possibility of representing the losses to the degree of accuracy obtained, in the form of a generalised equation, is of considerable value.

In considering these curves, it should be realised that the total power factor is

very small. Thus, at 10^5 cycles per second, on the curve for the capacity of 314 $\mu\mu$F, the resistance is seen to be 0·14 ohm, from which

$$\varphi_c = 2 \times 10^5 \times 314 \times 10^{-12} \times 14 \times 10^{-2} = 2{\cdot}75 \times 10^{-5}$$

Expressed as a phase angle, this quantity is equal to about 5″ of arc. In a circuit in which the whole power factor is 0·003 the condenser losses in such a case are about 1 per cent. of the total, so that an uncertainty of 10 per cent. in these losses would represent a quantity which is just about at the limit of measurement in the present state of the art of effective resistance measurement—i.e., one part in a thousand.

If the losses are expressed as power factors, then the results calculated by the equation (3) are as given in the following table :—

TABLE.

Frequency, cycles per second.	Power factor, parts in 10^6.		
	494 $\mu\mu$F	314 $\mu\mu$F	184 $\mu\mu$F
2×10^6	59·0	51·2	57·8
1×10^6	37·2	37·4	48·5
5×10^5	26·3	30·5	45·0
2×10^5	19·8	27·6	43·9
1×10^5	18·6	27·2	45·0
5×10^4	18·7	28·6	48·0
2×10^4	22·2	34·3	58·0

These results are shown by the dotted curves of Fig. 3. It will be seen that the

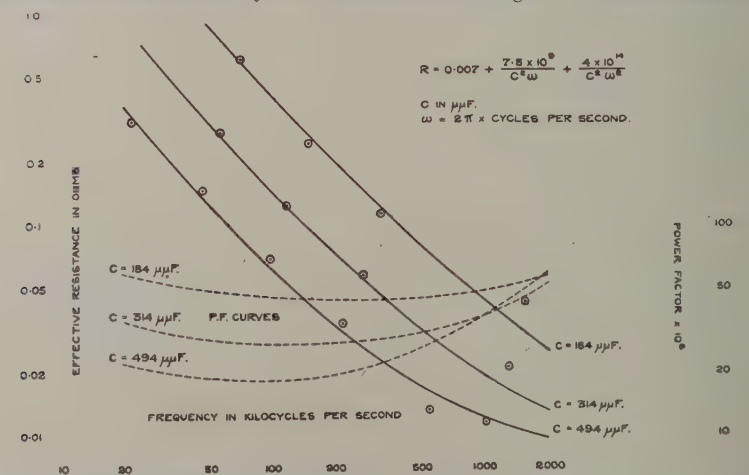


FIG. 3.—EFFECTIVE RESISTANCE AND POWER FACTOR CURVES OF STANDARD VARIABLE AIR CONDENSER.

power factor at a particular setting of the condenser is not very variable with respect to frequency over a considerable belt, but that it rises continuously for changes in each direction outside this belt.

The general consistency of the measurements made and the smallness of the

losses so found on the high class variable air condenser tested would appear to indicate that the use of a special air condenser, constructed in accordance with the principles and design of that described, can, in conjunction with a good variable air condenser measured by it, form a basis for effective resistance measurements of condensers and inductance coils to an accuracy at least as great as that which may be obtained by other methods at present available.

In the appendix which follows, calculations have been made of the probable maximum effective conductor resistance of the condenser based upon formulæ developed by Prof. Fortescue. It will be seen that the losses due to this cause are insignificant.

I am indebted to Messrs. Martin and Vigoureux for assistance in taking the observations, and to the latter for making the calculations given in the Appendix.

The work described in this Paper forms part of a programme carried out for the Radio Research Board, and is published by permission of the Department of Scientific and Industrial Research.

Appendix.

Calculation of Effective Resistance of the Conductors of the Condenser.

The calculations are based on the assumption that the current flow in the plates of the condenser follows the same law of propagation as that in a plane conducting surface of thickness large compared with the effective penetration of the current.

In such a case the effective resistance of an element of the path of length ds and width b is given by

$$dR = \rho m ds/b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ is the resistivity, ds and b are in the same units, and m is a factor for the penetration, having the dimensions of the inverse of a length. It is given by the well-known expression

$$m = 2\pi\sqrt{\mu n/10^9\rho}$$

where n is the frequency in cycles per second and μ is the permeability in such units that for a vacuum it has the value unity.

The frequency conditions are such that m is of the order 60, so that the effective penetration is only 1/6 mm. We must assume, therefore, that the current is confined to a very thin surface layer, and hence that the current flowing out from the lower surface of the insulated plate has first to travel radially outwards over the upper surface and round the edge.

Returning to equation (1), it is clear that the resistance of an annular element of radius r and width dr, is, with respect to the current actually traversing it, equal to

$$dR = \rho m dr/2\pi r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The total current traversing any element will vary continuously with the radius. In order to express the effective resistance in terms of the total current flowing, we must therefore multiply dR by I_r^2/I_0^2 where

I_r represents the current at radius r

and I_0 is the total current.

We can now deal with each portion of the condenser separately.

Referring to Fig. 1,

Let r_1 be the radius at which current enters the insulated plate system at the top of the copper block ;
r_2, the radius at which current leaves the copper block and enters the upper surface of the insulated plate P ;
r_3, the radius of plate P ;
r_4, the radius of hole in upper outer plate ;
r_5, the radius of upper and lower outer plates ; and
r_6, the radius at which current leaves lower outer plate.

For the upper flat portion of the copper block of effective resistance R_1 we have for the current I_0, which flows radially from r_1 to r_2,

$$R_1=\frac{\rho_1 m}{2\pi}\int_{r_1}^{r_2}\frac{1}{r}dr=A_1\log_e(r_2/r_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the cylindrical portion of the copper block of effective resistance R_2 we have for the current I_0 flowing down its length l at radius r_2,

$$R_2=k\,\rho_1 l/\pi {r_2}^2,$$

where $$k=856\sqrt{m_1}+0{\cdot}25,$$

and $$m_1=\frac{4}{3}\times 10^{-8}\times\mu n {r_2}^2/\rho.$$

For the upper surface of the insulated plate of effective resistance R_3 and of inner and outer radii r_2 and r_3, we have

$${I_r}^2/{I_0}^2=(2{r_3}^2-r^2)^2/(2{r_3}^2-{r_2}^2)^2,$$

where $$R_3=\frac{A}{B^2}\int_{r_2}^{r_3}(2{r_3}^2-r^2)^2dr/r,$$

$$R_3=(A/B^2)\ [4{r_3}^4\log_e r_3/r_2-2{r_3}^2({r_3}^2-{r_2}^2)+({r_3}^4-{r_2}^4)/4]$$

where $A=\rho m/2\pi$, and $B=(2{r_3}^2-{r_2}^2)$.

For the lower surface of the insulated plate we have

$${I_r}^2/{I_0}^2=r^4/B^2,$$

where $$R_4=\frac{A}{B^2}\int_0^{r_3}r^3dr,$$

$$=(A/B^2){r_3}^4/4$$

In a similar manner for the outer plates it will be found that the effective resistance R_5 of the under surface of the upper plate from radius r_4 to radius r_3,

$$R_5=(A/B^2)\ [({r_3}^4-{r_4}^4)/4-{r_4}^2({r_3}^2-{r_4}^2)-{r_4}^4\log_e(r_3/r_4)]$$

For the surfaces of the upper and lower outer plates lying outside the insulated plate, and comprised between the radii r_3 and r_5 the current has the constant value given by

$$I_r/I_0=r_3^2/B,$$

whence

$$R_6=(A/B^2)\,[2(r_3^2-r_2^2)^2\log_e r_5/r_3]$$

Finally, for the remainder of the upper surface of the lower plate, we have

$$R_7=(A/B^2)\,[B^2\log_e r_3/r_6-B(r_3^2-r_6^2)+(r_3^4-r_6^4)/4]$$

The following constants have been taken and calculations made for two sizes of insulated plate :—

$r_1=6$ mm., $r_2=19$ mm., $r_3=82$ mm. and 132 mm.

$r_4=21$ mm., $r_5=140$ mm., $r_6=6$ mm.

For the brass plates the value 9×10^{-6} has been taken for ρ. The calculations all refer to a frequency of 10^6 cycles per second :

$\rho m/2\pi=A=1\times10^{-4}$. Case I, $B=130$, Case II, $B=345$.

The values of resistance of the various parts for the smallest and for the largest plates calculated in microhms are as in Table I.

TABLE I.

Part of circuit.	Case I (small plate).	Case II (large plate).
R_1	45	45
R_2	62	64
R_3	112	154
R_4	7	6
R_5	6	6
R_6	27	4
R_7	215	265
Total (microhms) ...	476	544

It is thus seen that at the frequency 10^6 cycles per second the calculated conductor resistance of the condenser is of the order 0·0005 ohm., which is smaller than can be observed in the present state of resistance measurement.

The effective resistance so calculated is proportional to the square root of the frequency over the range of frequencies concerned.

XXXVIII.—A NOTE ON THE ACOUSTIC PRESSURE AND VELOCITY RELATIONS ON A CIRCULAR DISC AND IN A CIRCULAR ORIFICE.

By A. G. Warren, *M.Sc.*, *M.I.E.E.*, *F.Inst.P.*

Received June 15, 1928.

Abstract.

It is shown that at low frequencies the pressure at the edge of a rigid diaphragm, vibrating in a hole in a thin wall, is $2/\pi$ times the pressure at the centre (the case of the moving-coil loud-speaker). In the converse case of an acoustic wave impinging upon a circular orifice, the velocity increases towards the edge (the case of a resonator orifice). Were the medium non-viscous, an infinite velocity would be attained at the periphery.

IN a recent paper, Richardson* drew attention to the fact that in the orifice of an acoustic resonator the velocity increases towards the boundary. In the discussion which followed, the present writer suggested that an "annular effect" of this nature might be expected, in view of certain analogous effects which occur in the moving-coil loud-speaker. The explanation then suggested was substantially correct, although a defective recollection of the exact conditions obtaining at the edge of a vibrating disc led the writer to doubt at the time whether the explanation was complete.

It is proposed, therefore, to re-state briefly the conditions of both of these problems. Let us consider the conditions obtaining in the semi-infinite space on one side of an extensive wall A, of negligible thickness, in an aperture in which a diaphragm B vibrates harmonically (Fig. 1). If B is rigid we have the case of the

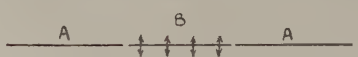


Fig. 1.

loud-speaker. The case of the orifice is obtained when B is extremely light and extremely flexible; we have then to determine the motion of its parts when a sound wave falls upon the wall.

Case (*a*), *B Rigid.*

The conditions are: The normal velocity (harmonic) v $(=-d\varphi/dn$, where φ is the velocity potential) is constant over the disc, and $d\varphi/dn=0$ over the wall.

It is easy to show that at the centre of the disc

$$\varphi=(iv/k)(1-\cos kR+i\sin kR) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the pressure

$$p=a\rho v(1-\cos kR+i\sin kR) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(where $k=\omega/a$, $\omega=2\pi\times$frequency, a is the velocity of sound, ρ the density and R the radius of the disc.)

* The Amplitude of Sound Waves in Resonators, Proc. Phys. Soc., May 11 (1928).

Similarly, at the edge of the disc

$$\varphi=(iv/2k)\{1-J_0(2kR)+i\,.\,K_0(2kR)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$p=\tfrac{1}{2}a\,\rho v\{1-J_0(2kR)+i\,.\,K_0(2kR)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The pressure has two components, one in phase with the velocity, responsible for the acoustic output, and one in phase with the acceleration, expended in overcoming inertia forces. At low frequencies (wave-length great compared to diameter of disc) we may write

$$p_{(\text{centre})}=a\,\rho v(k^2R^2/2+ikR) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$p_{(\text{edge})}=a\,\rho v(k^2R^2/2+ikR\,.\,2/\pi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The acoustic pressure is uniform over the disc, but the inertia pressure falls towards the edge. It is clear that as the frequency falls the inertia pressure becomes increasingly great compared with the acoustic pressure (for instance, for a disc of 10 cms. radius at a frequency of 27·2, the acoustic pressure is 0·00125 $a\rho v$, while the inertia pressure at the centre is 0·0500 $a\rho v$, and at the edge 0·0318 $a\rho v$). For frequencies at which we may assume that the phase lag in transmission over the face of the disc is negligible, we may write

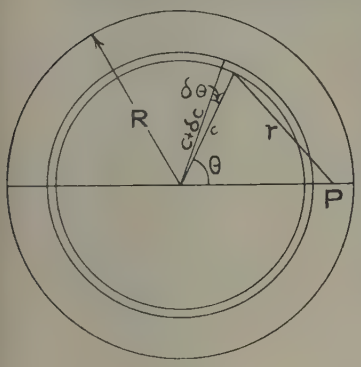


FIG. 2.

$$p_{(\text{centre})}=ia\,\rho vkR \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$p_{(\text{edge})}=ia\,\rho vkR\,.\,2/\pi \quad . \quad . \quad . \quad . \quad (8)$$

limited equations which may be derived by direct integration.

It is seen that the pressure at the edge of the disc is 0·617 of the pressure at the centre.

Case (b), B Flexible, a Sound Wave Impinging upon it.

Owing to the symmetry on the two sides of the aperture, it is clear that the motion of the air in the aperture must be normal to the plane of the wall. Hence the conditions are: φ constant over the aperture, $d\varphi/dn=0$ over the wall, and φ constant at infinity.*

Let the velocity at a radius c be $u=f(c)$. Then the potential at a point P distant a from the centre (Fig. 2) is

$$\varphi=-\frac{1}{\pi}\int_0^R f(c)\int_0^\pi \frac{e^{-ikr}}{r}\,d\theta\,.\,dc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$r=\sqrt{a^2+c^2-2ac\cos\theta}.$$

To satisfy the conditions, $f(c)$ must be found such that φ is independent of a. The general solution is almost impossible. When, however, the frequency is low,

* Rayleigh, Theory of Sound, Vol. 2, p. 176.

we may make similar approximations to those made in case (*a*)—i.e., write $e^{-ikr}=1$. The first integral then becomes an elliptic function; even then considerable labour is involved in showing that

$$u=f(c)=vR/\sqrt{K^2-c^2} \quad \ldots\ldots\ldots\ldots \quad (10)$$

is a solution.

Fortunately for low frequencies, a much simpler solution is possible, based upon a method used by Rayleigh* in determining the conductivity of an elliptical orifice. In fact, the result here obtained is latent in Rayleigh's analysis of that case.

The general acoustic problem is the same as that of the determination of the distribution of electric charge upon a circular disc whose potential varies harmonically. When the radius of the disc is comparable with the wave-length the solution of this problem is difficult. It is simple, however, when the disc is small;

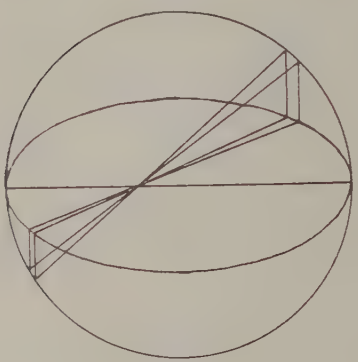


Fig. 3.

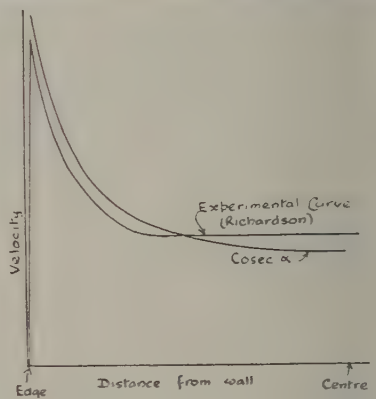


Fig. 4.

the distribution is then the same as in the static case. This is simply determined as follows: The distribution of charge on an isolated sphere is uniform, and no force is exerted at any point within it. Consider the vertical diameter to shorten so that the sphere becomes a spheroid (Fig. 3). Clearly, there will still be no force exerted at an internal point if the horizontal distribution of charge remains unaltered. Finally, let the sphere collapse to a disc, and we see that the charge density at a point distant a from the centre is proportional to cosec α, where $\cos\alpha=a/R$. The velocity distribution in an acoustic orifice is similar.

This indicates that an infinite velocity is required at the edge of the orifice to make φ uniform. Viscosity, of course, renders the velocity zero at the extreme edge, and limits the maximum velocity attained.

It is interesting to compare the theoretical distribution of velocity, neglecting viscosity, with one of Richardson's curves (Fig. 4).

* Ibid.

DISCUSSION.

Dr. E. G. RICHARDSON: The theorems of Rayleigh mentioned by Mr. Warren in regard to the "conductivity" of and flow through an orifice are based on static and continuous current electrical analogies. They contain no frequency term and should be equally applicable to continuous flow through an orifice. The infinite velocity at the edge which Rayleigh's equations give is the stumbling-block that Helmholtz and others encountered in theoretical hydrodynamics for the flow past a sharp edge. The fact is that alternating flow does give a high velocity at the edge of the "boundary layer" along the wall, whereas continuous flow through such an orifice shows a gradually falling velocity from the centre to the edge. It may be possible to describe the former motion by the introduction of inertia terms such as those which Mr. Warren has demonstrated for the case of the plate.

AUTHOR'S reply: I think it is hardly correct to say that the theorems of Rayleigh commented upon in the paper are based upon static and continuous current electrical analogies. At low frequencies the analysis of the orifice is the same as that of the determination of the potential in a particular electrostatic case. (As Rayleigh says, the problems are *mathematically the same.*) Between the two problems, one static and the other harmonic, there is, however, no very obvious physical analogy. All the equations and reasoning in the paper are applicable only to the acoustic (harmonic) case; the variables are instantaneous values in a harmonic variation, and cannot be interpreted otherwise. The essential feature of the problem is a time variation; then, when the frequency is low (the velocity being necessarily high), the inertia, or out-of-phase pressure is the only component. To attempt to reduce the frequency sufficiently to cover steady flow renders all the equations indeterminate. With the case of continuous flow I am not particularly concerned, but I cannot see any inconsistency between the facts of such flow and the facts of harmonic flow experimentally determined by Dr. Richardson and suggested by Rayleigh's analysis. No doubt a comprehensive treatment would cover both cases, but it is only the harmonic case which was under discussion.

I do not gather the import of Dr. Richardson's final sentence. I hoped that I had shown that the problems of the plate and orifice were fundamentally similar, and that high velocities near the edge of the orifice would be expected. The apparent difference of treatment of the two cases was the result of an inability to solve equation (9) in general terms.

XXXIX.—VARIATIONS IN THE FINE STRUCTURE OF H_α.

By G. E. Harrison, *Ph.D.*

Received May 26, 1928.

Abstract.

The present paper describes the results of an attempt to study the intensity changes taking place in the fine structure of $H\alpha$ with alteration of the bore of the discharge tube at constant gas pressures and current densities. The large variations in the electric field surrounding an emitting particle are concluded to account for the observed changes in the intensity distribution which amounted to 100 per cent. The doublet separation, however, appeared to be independent of these changes, the mean value obtained being 0·304 cm.$^{-1}$.

Introduction.

THE work of Hansen,* Houston† and Gehrcke and Lau‡ has shown that the well-known fine structure components of the Balmer lines of hydrogen are subject to intensity variations which depend upon the gas pressure and current-density within the discharge tube. In these investigations, however, the changes observed were produced by varying the pressure and current within a tube of fixed diameter.

The observations made by Wood§ and by Merton‖ have revealed the great influence exerted on many spectral intensity distributions by the proximity of the radiating gas to solid surfaces, such as the walls of the tube. The present paper describes an attempt, therefore, to study the intensity changes in the fine structure taking place at fixed pressures and current densities, with alteration of the bore of the discharge tube. The results reveal the predominating effect of this variation upon the intensity distribution, and are of further interest in view of the fact that the old quantum mechanics appears to offer an inadequate explanation of the observations.

Experimental.

A discharge tube two feet long bent twice at right angles was employed. The central portion of the tube consisted of three pieces of capillary of 0·1, 0·16 and 0·2 cm. bore respectively, each about two inches long, and joined end to end. A McLeod gauge was connected to this tube, so that observations of the gas pressure could be made. Commercial hydrogen was admitted from a reservoir attached to the apparatus.

A Fabry-Perot interferometer used as an étalon was employed in the present experiments. The rear plate was carried upon a sliding block, the position of which was controlled by a good screw. It was found that temperature changes producing variations in the distance between the plates considerably affected the diameter of the interference fringes. The instrument was therefore enclosed in a double-walled metal cover, consisting of four sides and a detachable top. The space between

* Hansen, Ann. d. Phys., 78, p. 588 (1925).
† Houston, Astro. Phys. Journ., 64, p. 81 (1926).
‡ Gehrcke and Lau, Ann. d. Phys., 65, p. 575 (1921).
§ R. W. Wood, Phil. Mag. (6), 44, p. 538 (1922).
‖ Merton, Proc. Roy. Soc. (A), 97, p. 307 (1920).

these walls was filled with water at room temperature, while the outer surfaces were covered with felt. The temperature changes within this enclosure corresponded to a rate of change of ring diameter of 1 per cent. per hour. Provision was made at either end of the cover for the insertion of a tube, the first one carrying the collimation system, and the other the photographic objective and dark slide.

The collimating tube carried a fixed slit $1'' \times 0{\cdot}06''$ at the one end, opposite which the discharge to be studied could be placed. A Wratten *F* filter transmitting radiations between 6100 and 7600 Å. was mounted at the other. As the H_α line was always considerably stronger than the lines of the secondary hydrogen spectrum, the transmitted radiation was found to be adequately monochromatic. The collimation lens was of 5 cm. focal length, set to converge a narrow cone of light upon the rear interferometer plate. As described by Fabry and Buisson,* the parallelism between these plates was improved by mounting a fixed circular diaphragm of about 0·6 cm. in diameter immediately in front of them.

It may be shown that the distance between the fringes due to two radiations separated by a spectral range of 0·14 Å. is a maximum when the interval between the silvered surfaces of the interferometer plates is 0·75 cm. The fringes due to the respective radiations then lie exactly half-way between one another and the

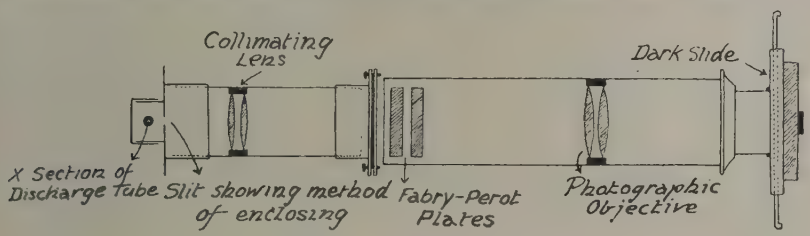


Fig. 1.—Diagram of Optical Apparatus.

instrumental corrections are a minimum.† This interval was kept constant throughout the experiments.

A Beck isostigmat photographic objective of 15 cm. focal length was mounted in the second tube in such a position that parallel rays were focussed in the plane to be occupied by the photographic plate. The dark slide was constructed so that two comparison exposures could be made upon a single plate. The general arrangement of the apparatus is shown in Fig. 1.

A large induction coil fitted with a rotary break was used to excite the discharge tube. The primary potential was 40 volts, and the secondary currents varied from 1 to 10 milliamperes. At the higher currents the rectification was very incomplete. A mechanical rectifier which was found to be efficient and of negligible resistance was therefore fitted to the mercury break.

The intensity distribution in the fine structure was measured by a photo-electric microphotometer. The constructional detail of this instrument was similar to that described by Koch.‡ In the present measurements, however, the area of illumina-

* Astro. Phys. Journ., 28, p. 169 (1908).
† C. Van Cittert, Ann. d. Phys., 77, p. 379 (1925).
‡ Ann. d. Phys., 39, p. 705 (1912).

tion upon the photographic plate under investigation was limited in length by the curvature of the interference fringes. It did not, therefore, exceed 0·00002 sq. cm., or about 1/50th of that employed in previous microphotometric measurements. The photo-electric current which was of the order of $0{\cdot}2\times10^{-10}$ ampere was obtained by observing the rate of growth of charge upon a pair of Dolezalek electrometer quadrants. This was controlled by increasing the capacity of the electrometer with a suitable fixed condenser. Correction was made for the dark conductivity of the photo-electric cell, which was found to vary from day to day, and also to decrease after the cell had been rested for several hours. Consistent results were obtained with this microphotometer when due precaution had been taken with the electrostatic insulation and the removal of water vapour from the surfaces of the cell and the electrometer.

The photo-electric current was calibrated with a photographic wedge and found to be accurately proportional to the intensity of the light incident upon the cell. The density of the photographic image was deduced from the relationship

$$D=\log_{10}\left(\frac{\text{Intensity of light incident upon plate}}{\text{Intensity of light transmitted}}\right).$$

The intensity of the fine structure components was assumed to be proportional to the density of the respective fringes recorded upon the photographic plate for a given time of exposure.

Photometric observations were made along a ring diameter. The minimum recorded between consecutive orders of interference was taken as the zero. The intensity of the fine structure components was then obtained from the resulting curves by subtracting this zero intensity from that of the respective maxima. The half-intensity line was deduced for each component and the mid-points calculated. The correction employed by Hansen for the partial fusion of two radiations of approximately equal intensity was applied, and the " true separation " of the mid-points obtained.

Although photographs of the fine structure were taken over a pressure range from 1·1 to 0·09 mm. Hg, and at current densities ranging from 13 to 86 milliamperes/sq. cm., the intensity ratio I_s/I_L for the two observed components of H_α (where I_s, I_L are the intensities of the short-wave and long-wave components respectively) were quite different from those obtained by Hansen. The long-wave component was always much the stronger. Thus, in the tube of 0·16 cm. bore, the intensity ratio I_s/I_L increased from 0·49 to 0·64, as the gas pressure was lowered from 0·93 to 0·097 mm. Hg. These results led to the conclusion that the diameter of the discharge tube had a considerable influence upon the intensity distribution in the fine structure.

To investigate this dependence, two further discharge tubes were constructed. These were exactly similar in design to the first one. The central portions, however, consisted of three pieces of capillary tubing joined end to end, of internal diameters 0·27, 0·34, 0·45 cm., and 0·5, 0·6 and 0·7 cm. respectively. Comparison photographs were taken at similar gas pressures and current densities to those employed in the first experiments.

For the widest bore (0·7 cm.) an intensity distribution was obtained in which the short wave component was considerably enhanced. In agreement with Hansen's results, this component was the stronger at low pressures. The intensity distribu-

tions in the case of tubes of about 0·5 cm. diameter, a specimen of which is shown in Fig. 2, were intermediate between those already discussed.

As a further test of the effect of the bore of the discharge tube upon the fine structure another system of tubes was constructed. This apparatus consisted of a central portion bounded by two tubes of 0·5 and 0·6 cm. internal diameter, fixed axially and in communication with a third tube of 0·9 cm. bore. The space between the central tube and the outer one was about 0·1 cm. A discharge could be established in the inner tube or in the interspace between the inner and outer portions independently. In the former the intensity distribution at a given pressure was similar to that obtained for the wider bores in the previous experiments, the intensity ratio (I_s/I_L) being about 0·97 at a pressure of 0·1 mm. Hg. In the latter case the ratio was about 0·6 at the same pressure and current density. It should be stated, however, that, owing to the imperfect axial alignment of the inner and outer tubes, the discharge took the path of least cross-section, and thus only about one-third of the interspace was excited. The results, nevertheless, afford further evidence of the effect of the proximity of the tube walls upon the fine structure.

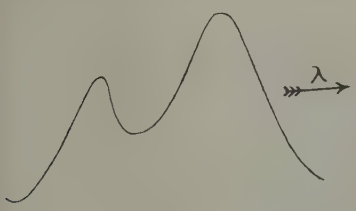


FIG. 2.—INTENSITY DISTRIBUTION IN THE FINE STRUCTURE $H\alpha$.
Tube bore 0·45 cm., gas pressure 1·02 mm. Hg, current-density 11·8 m. amps/sq. cm.

TABLE OF RESULTS.

Tube width, cm.	Current density, m.amps./sq. cm.	Pressure, mm. Hg.	Intensity ratio (I_s/I_L)	Doublet separation, 8ν cm.$^{-1}$
0·162	33·0	0·93	0·49	0·305
	34·9	0·37	0·53	0·309
	34·0	0·097	0·64	—
0·203	21·1	0·94	0·57	0·309
	22·4	0·36	0·66	0·304
	21·7	0·099	0·70	0·306
0·272	30·3	0·56	0·68	0·301
	29·8	0·89	0·77	0·297
0·344	20·3	1·01	0·66	0·298
	19·0	0·57	0·69	0·304
	18·3	0·087	0·81	0·297
0·45	11·8	1·02	0·67	0·306
0·49	36·4	1·10	0·69	0·301
	35·6	0·55	0·76	0·297
	28·9	0·153	0·89	0·307
0·68	18·4	1·10	0·73	0·304
	18·3	0·55	0·76	0·300
	14·3	0·153	1·07	0·305

Mean separation of the mid-points of the components $(\delta\nu) = 0{\cdot}304 \pm 0{\cdot}005$ cm.$^{-1}$.

Specimen photographs of the fine-structure of H_α showing the large variations in the intensities of the two components are shown in the accompanying prints. The component of longer wavelength is situated nearer the centre of the interference pattern in each order.

Conclusion.

(*a*) *Experimental.*

(i) The intensity ratio (I_s/I_L) increased with the diameter of the discharge tube. If I_R represents the reciprocal of this ratio, then at a given gas pressure and current density the observations appeared to be approximately satisfied by the formula

$$I_R = a/d^2 + c$$

d being the internal diameter of the discharge tube and a and c constants depending upon the pressure and current density.

(ii) In a given tube operated at a constant current density, the intensity ratio (I_s/I_L) increased as the pressure decreased. This result is in qualitative agreement with Hansen's observations, but the variations in the intensity distribution are much larger.

(iii) The mean value obtained for the doublet separation was 0·304 cm.$^{-1}$. Re-measurement of Schrum's plates by Janicki* yielded the value 0·302 cm.$^{-1}$, while the same investigator obtained the value 0·306 cm.$^{-1}$ from the plates taken by Gehrcke and Lau.†

On the other hand, Hansen, Houston and Kent, Taylor and Pearson‡ all obtained the higher value of 0·316 cm.$^{-1}$, these results all being deduced from photometric measurements.

(iv) The doublet separation remained practically constant throughout the whole series of experiments. For a given tube, it appeared that the separation of the doublet was greater when the current density was reduced, in agreement with the observations of Hansen and Houston. This variation was, however, within experimental error.

(v) While Hansen observed an asymmetry only in the short wave component, in the present experiments the asymmetry was in general common to both of the observed radiations.

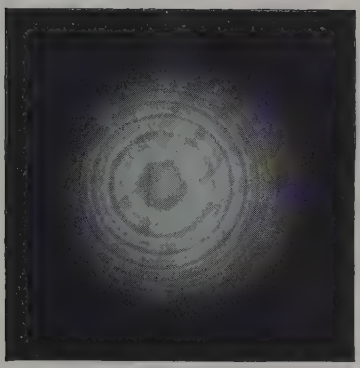
(*b*) *Theoretical.*

The bore of the discharge tube evidently exerts a predominant effect upon the intensity distribution in the fine structure. This is attributed to a variation of the electric field surrounding an emitting particle in the positive column brought about in the three following ways :—

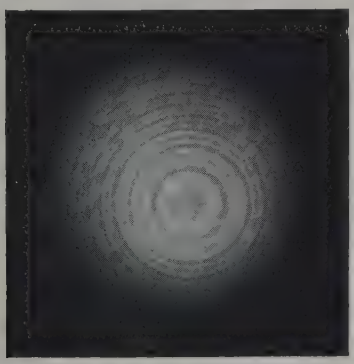
(i) The general electric field in the positive column is accounted for by the space charge and the charge carried upon the walls of the discharge tube. Any change in the diameter of the tube will therefore bring about a modification in both of these variables, and the change will be most evident in the case of narrow tubes. The field in the neighbourhood of a radiating particle will therefore be largely increased by changing from a wide to a narrow bore.

(ii) The work of R. W. Wood has familiarised us with the strong catalytic action of the glass walls of a discharge tube. This results in the formation of

* Ann. d. Phys., 76, p. 561 (1925).
† Zeit. f. Phys., 35, p. 1 (1925).
‡ Nature, Vol. 119, Jan. 29 (1927).



Tube Bore 0·20 cm., Gas Pressure 0·36 mm. Hg.,
Current Density 22·4 m.amps./sq.cm.



Tube Bore 0·68 cm., Gas Pressure 0·153 mm. Hg.,
Current Density 14·3 m.amps./sq.cm.

To face page 304]

molecular hydrogen by re-combination of the dissociated atoms. A high concentration of molecular hydrogen is therefore to be expected upon the tube walls resulting in a strong inter-molecular field. The proximity of this field to an excited particle depends upon bore of the discharge tube.

(iii) The mean free path of a hydrogen atom at 0·5 mm. Hg is about 0·6 cm. This will be considerably decreased in the case of the narrow tubes employed in the present experiments. This will result in an increased number of collisions, and thereby an increased electric field surrounding a radiating particle.

Variation in the electric field in these three ways, with alteration of the bore of the discharge tube, is concluded to produce the predominant intensity changes observed in the fine structure.

If the gas pressure rises within a discharge tube the general electric field is also increased. The pressure change may, however, be due to two different effects.

A mechanical increase of pressure represented by the admission of gas into the discharge tube will raise the concentration of charge within the tube, and thus increase the general electric field. Alternatively, an increase of pressure may be due to molecular dissociation. The more molecules dissociated the greater the concentration of free particles, and thus the higher the pressure. This type of pressure change will give rise to an increase of the electric field through variation of the number and kind of free charges.

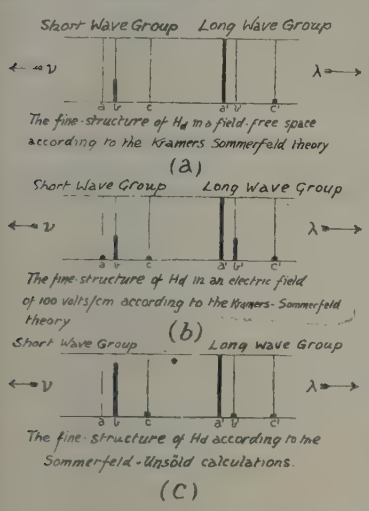

Short Wave Group
Long Wave Group
ν
λ
a b c a' b' c'
The fine-structure of Hα in a field-free space according to the Kramers Sommerfeld theory
(a)
Short Wave Group
Long Wave Group
ν
λ
a b c a' b' c'
The fine-structure of Hα in an electric field of 100 volts/cm according to the Kramers-Sommerfeld theory
(b)
Short Wave Group
Long Wave Group
ν
λ
a b c a' b' c'
The fine-structure of Hα according to the Sommerfeld-Unsöld calculations.
(c)

FIG. 3.

An increase of current-density brings about an increased concentration of free charges, which in turn will lead to a more intense field within the discharge tube.

Combining the Bohr quantum theory of the emission of spectral lines with the relativity variation of mass with velocity, Sommerfeld has calculated the position of the six possible fine structure components for H_α shown as a, b c, a', b', c' in Fig. 3.

H. A. Kramers* found that the Bohr selection principle limited the number of "allowed components" to three in a field free space. The intensity distribution is that obtained in Fig. 3(*a*). Extending this investigation, Kramers calculated that, for a field of 100 volts/cm., the intensity distribution was modified to that shown in Fig. 3(*b*).

Sommerfeld and Unsöld† have recently extended the analogy between the hydrogen spectrum and that of the alkalis. They have thus re-calculated the position and intensity of the allowed five structure components, using the alkali-like numbering of the quantum levels, together with the intensity rules due to Burger and Dorgelo. The results are indicated in Fig. 3(*c*).

Kramers' calculations based upon the original Sommerfeld theory lead to a

* Zeit. f. Phys., 3, p. 221 (1920).
† Zeit. f. Phys., 36, p. 259 (1926).

doublet separation not less than 0·329 cm.$^{-1}$, a value which is not supported by any recent photometric measurement. It appears, as pointed out by Houston, that this theory is inadequate.

The intensity distribution obtained by Sommerfeld and Unsöld undoubtedly agrees more closely with that found in practice. The doublet separation (0·320 cm.$^{-1}$) again appears to be too large, while the calculated intensity ratio (0·8) is supported by experimental evidence only under certain discharge conditions.

The observed asymmetry of the short wave component is in contradiction to all three calculations. It may safely be concluded that this asymmetry is due to the excitation of the c component. This agrees with Hansen's conclusions, and with the observations of Kent, Taylor and Pearson. But in order to account for this asymmetry the intensity of the c component must be concluded to be appreciable compared with a and b, certainly greater than that given by any of the three calculations.

Hansen supposes that the pressure variations in the intensity ratio are due to changes in the b' component, brought about by alteration of the electric field. The Kramers-Sommerfeld calculations would lead to the conclusion that while the intensity of a' is not materially altered by variation in the electric field, the intensity of c' is small compared with that of a'. Following Hansen, therefore, variations in the intensity ratio taking place with tube bore or gas pressure, which in the present experiments reached 100 per cent., are to be attributed to changes in the intensity of b'. Such large variations in a single component would presumably lead to changes in the doublet separation, and this is not supported by any experimental evidence. It is probable, therefore, that the intensity changes accompanying a variation of the electric field in the neighbourhood of an emitting particle take place in components of both groups, certainly in more than a single fine-structure component.

The variations in the intensity ratio of the fine structure doublet are concluded, therefore, to be due to the changes of the electric field accompanying a change of tube bore, gas pressure or current density. That the present theory is incapable of affording an adequate explanation of the phenomenon observed is not surprising when one considers the character of the fields of rapidly changing strength and direction, which act upon any emitting particle in a discharge tube. The observed gas pressures and current densities are, moreover, only averages over the whole tube. The actually field in the neighbourhood of an emitting particle is probably very different at any given instant from that calculated from these observations.

The most recent developments in atomic physics show that the model by means of which the fine structure has hitherto been calculated must be abandoned. The calculation must be made with quantum mechanics instead of classical mechanics, together with the modification due to spinning electrons. Heisenberg and Jordan* have shown that, as a result of these compensating modifications, exactly the same Sommerfeld possible fine structure levels are obtained. The difference between the results derived from the new and old calculations must therefore be confined to the intensities of the allowed components. Whether the new theory will explain the experimental facts is, as yet, a matter for conjecture.

In conclusion, I would like to thank Professor S. W. J. Smith, F.R.S., for the ready facilities he has provided for the carrying out of this work, and Mr. M. C. Johnson, M.A., for his helpful advice and criticism. I am also indebted to Mr. G. O. Harrison for the construction of the discharge tubes.

* Zeit. f. Phys., 37, p. 263 (1926).

XL.—A SIMPLE GOLD-LEAF ELECTROMETER FOR HIGH-FREQUENCY MEASUREMENTS.

By Satyendranath Ray, *M.Sc.(Cal.)*, *B.Sc.(Eng.)(Lond.)*.

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(*Communicated by* Dr. D. Owen.)

Abstract.

A gold-leaf electrometer of the attraction type has been designed to supply the need for a simple instrument that can be used to measure voltages down to a few volts in high-frequency circuits, and which permits of precise indications of exact resonance in a simple circuit containing inductance and capacity.

The fixed element is a metal plate covered with a thin sheet of mica. The moving element is a narrow strip of gold leaf stiffened with a very light, tubular glass fibre extending almost up to the point of suspension of the leaf. The lower end of the glass fibre serves as the pointer. Simple means are provided for varying the sensitivity between wide limits.

The instrument will detect voltages as low as 4 volts and has a low capacity (2 to 4 micro-micro-farads). It also possesses the advantages of quick response and negligible power consumption. Instances of its application are given.

§1. Preliminary.

THE instrument here described was designed to meet the necessity which exists in certain high frequency tests of detecting and measuring the current in, or voltage across, a part of a circuit.

An instrument for this purpose should conform as closely as possible to the following requirements :—

1. Adequate sensitiveness.
2. Quick response—i.e., low period combined with large damping of the moving element.
3. Low power consumption.
4. Readings independent of frequency.
5. Minimum interference with the constants of the circuit into which it is introduced.

It should also be as simple and portable as possible.

The consideration that electrostatic instruments are inherently free from frequency errors and low in power consumption determined the choice of type of instrument.

The simplest arrangement of an electrostatic instrument consists of a fixed element close to a moving one which it attracts. For simplicity and constancy gravity control is incomparably the best. In an instrument so controlled the force between the two elements is, for a given potential difference, proportional to the rate of change of capacity of the system with displacement. This capacity is, therefore, necessarily variable, and as such variation must be kept as low as possible to satisfy condition (5) above, the couple of attraction must also be small. To retain adequate sensitiveness the restoring couple, which is due to gravity, in its turn must be small ; hence the weight of the moving system must be as small as possible.

After trial of thin foils of different metals, gold leaf was chosen for the combined advantages of lightness and perfect flexibility at the hinge when freely suspended. The flexibility of the leaf as a whole is, however, a disadvantage, and it was accordingly decided to stiffen it with the lightest glass fibre that could be conveniently drawn and handled, and that would yet cause the gold leaf to move practically as a rigid body. In this way perfect definiteness of reading for a given potential difference was secured, with not too great a sacrifice of sensitivity.

§2. Description of Instrument.

Referring to Fig. 1, the instrument as finally constructed consists of a cylindrical case *A* closed by two windows, the back window of ground glass and the front one of clear glass. The case has two concentric grooves *HH* cut in it which can move along two semi-circular runners *RR*.

The fixed element is a brass plate *P* 20 mm. long and 5 mm. wide, covered with

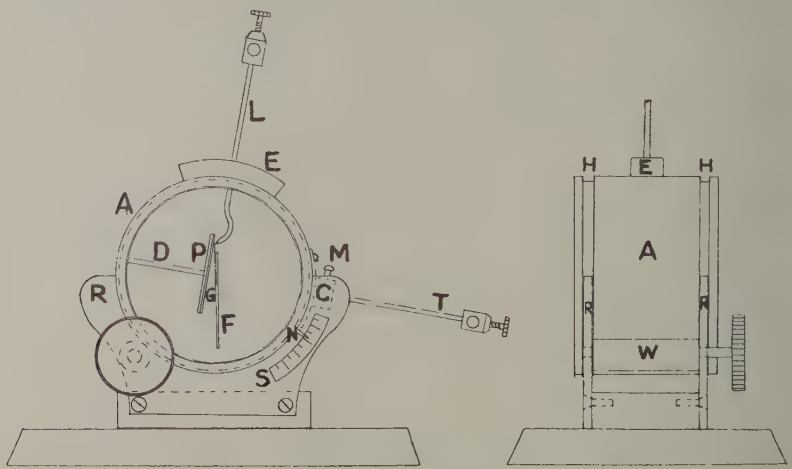

Fig. 1.—Front and Side Elevations of Instrument.

a mica film 0·01 mm. thick, attached with shellac varnish. This mica slip serves to protect the moving element from direct contact with the plate. Where the case is of metal the plate is in metallic connection with the case.

The moving element is a strip of gold leaf *G* about 1 mm. wide and 15 mm. long, attached to a thick brass wire *L* which passes through an ebonite block fixed on the case, and carries an external terminal. The leaf is stiffened with a fine tubular glass fibre *F* about 0·05 mm. in diameter and 25 mm. in length, weighing about 0·08 mgm. The total weight of the moving part is thus approximately 0·12 mgm. The gold leaf, which hangs vertically when at rest, is very nearly, but not quite, in contact at its point of suspension with the mica slip covering *P*. The lower part, owing to the tilt of the plate, is farther away from it. The case can be turned in the grooves and runners by the aid of a friction wheel *W*. By this means the angle of tilt between the plate and the leaf when at rest can readily be adjusted according to the sensitivity

required ; the value of the tilt in degress being read off on the scale S by means of a pointer N fixed to the case. The instrument is held in the runners by two semi-circular spring clips not shown in the drawing.

The rod T serves as the terminal for the plate side of the instrument. It slides in a collar C fixed to the case, so that when pushed home and tightened with a set screw M it serves as a clamp for the leaf during transport.

Another model has been constructed with a fibre case, and in this the terminal for P is on the continuation outside the case of the rod D, the leaf terminal being on L as before.

§3. Characteristics of Instrument.

Sensitivity, Range and Calibration.

The sensitivity and range can be widely varied according to the thickness of glass fibre and the width of gold leaf used. With any one instrument the sensitivity can be adjusted within wide limits by altering the tilt of the plate.

Voltages as low as 4 volts can be observed with a tilt of 3 degrees. For such indication unaided visual observation is sufficient with ordinary illumination of the back window.

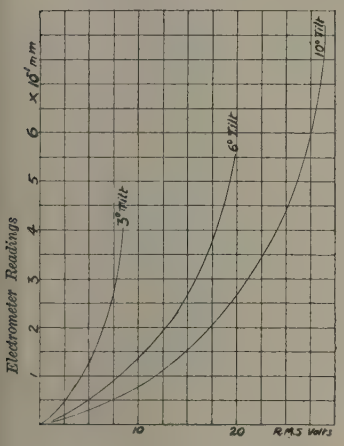

Fig. 2.—Calibration Curves.

For accurate measurement the instrument may be used with a low-power microscope (magnification, say, 10 diameters) ; with eyepiece scale divided into tenths of a millimetre deflections may be estimated to 1/100 mm. Calibration curves for the instrument as described in Section 2 are given in Fig. 2. From these it will be seen that with a tilt of 6° a potential difference of 15 volts can be measured to 1/5th of a volt—that is, with an error of less than 1·5 per cent.

Over the lower portion of the range of voltage the graph for any given angle or tilt approximates to a square-law calibration, but over the upper portion the curve rises more steeply. This latter represents the most sensitive region, and beyond this the point of instability is reached, at which the leaf is drawn up against the plate.

In the early stages of the work considerable trouble was experienced owing to the gold leaf adhering to the mica facing on the plate, from which it was hard to dislodge it without damage. After trial of various materials, it was found that fine talc powder dusted lightly on to the plate prevented stiction. This device works very well even in damp weather, only slight tapping being necessary, even at the worst of times, to free the gold leaf should it be drawn up to the plate.

The calibration is very constant, and no zero error is perceptible even after months of continuous work. This is the great advantage secured by the choice of a control which is almost solely due to gravity. Calculation shows that the restoring moment due to the flexure of the gold leaf at the hinge is not more than 1/200 of that due to gravity.

The instrument, like all sensitive idiostatic instruments, is preferably calibrated with alternating voltages, thereby eliminating the trouble due to contact electromotive forces when direct voltages are used. In the present instrument, with gold against brass, this electromotive force varies from day to day, but is of the order of 1·5 volts. This effect is, of course, without influence on alternating-voltage measurements.

Period and Degree of Damping.

The period of the moving system is well under half a second. The air damping is considerable, and causes the instrument to be almost dead beat. Actually, in the model described, on applying a voltage the pointer goes past the new resting-point but once, and that by less than 1/25 of the final deflection.

Capacity.

In the instrument with the brass case the capacity varies from 4·5 $\mu\mu$F at a tilt of 3° to 4·0 $\mu\mu$F at a tilt of 20°. In the model with a fibre case the capacities in these two positions are 2·0 and 1·5 $\mu\mu$F respectively.

§4. Example of Application.

To illustrate the behaviour and advantages of this leaf electrometer a brief account of its use in obtaining resonance curves may be given. Owing to the form of the calibration curves, the instrument readings plotted against another variable (e.g., condenser readings in a simple resonant circuit) give a curve with a distinctly more pronounced peak than even the square of the voltage plotted similarly. This effect becomes the more marked the nearer the approach to the point of instability of the leaf. With the milled head provided it is quite easy to adjust the tilt of the plate so that at the maximum voltage the leaf is near the verge of instability. When under these conditions the instrument is used to indicate resonance in a simple tuned circuit, or the crevasse in the quartz piezo-electric resonator circuit, sharp cusps appear on the curves, and the condenser settings for resonance can be reproduced with a precision limited usually only by the accuracy with which the condenser scale can be read. This is illustrated by the full curve given in Fig. 3.

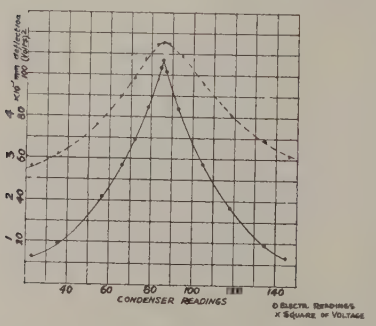

Fig. 3.—Resonance Curves.

For example: A variable condenser of maximum capacity 74 $\mu\mu$F, with dial divided into 180°, was used in parallel with a 250 $\mu\mu$F condenser. The resonance setting on the scale of the smaller condenser could be repeated to within 1/5th of a degree (the limit of error of reading of the scale). The resonance capacity was, therefore, determinable with an error of only 1 in 4,000.

Owing to the very quick response of the leaf, it is impossible to miss the peak, in the one case, or the crevasse in the other, even when the condenser dial is being turned rapidly.

The entire freedom of this instrument from time-lag, and the practically negligible power consumption constitute very appreciable advantages over the

thermo-element and micro-galvanometer usually employed in resonance-circuit measurements.

There is, moreover, a third advantage in such measurements arising from the combination of superior sensitivity with small power consumption, namely, that a much lower degree of coupling to the exciting circuit is possible. To illustrate this the following data may be quoted. In a circuit oscillating at $10^6 \sim$, with a $200 \mu\mu$F condenser in circuit, the instrument will indicate resonance sharply when the resonance voltage is 6 volts. This corresponds to a current of only 7·5 milliamperes in the circuit. If the high frequency resistance of such a circuit be taken as 8 ohms, the introduction of a heater element flattens the resonance curve, and, assuming its resistance to be 4 ohms, the maximum current to be detected falls to 5 milliamperes; or, alternatively, for the same current the coupling has to be made 50 per cent. stronger.

In conclusion, acknowledgments are due to the authorities of the Sir John Cass Technical Institute for facilities provided, and grateful thanks to Dr. D. Owen for his interest and guidance all through the work.

XLI.—THE STRUCTURE OF THE INDUCTION SPECTRA OF RARE GASES—ARC SPECTRA OF ARGON, KRYPTON AND XENON.

By Adolfo T. Williams, *Sc.D.*, Professor of Physical Chemistry, Instituto de Fisica, Universidad de La Plata.

Received May 12, 1928.

Abstract.

The purpose of this paper is to establish the usefulness of the excitation by induction method to separate different orders of the spectra of rare gases. The arc spectra are examined, constant separations and groups of lines deduced from Bloch and Dejardin's results, and the regions occupied by different series are established, and also the correspondence between theoretical terms and Meissner's terms in the arc spectrum of argon.

I. Arc Spectrum of Argon.

THE groups of lines deduced from Bloch and Dejardin's numerical data[1] do not agree with the series recently established by Meissner[2]. We have classified with Meissner's terms two new lines, 3354·3 ($1s_3$–$6p_8$) and 3355·4 ($1s_3$–$6p_9$), the residuals ($O-C$) in wave numbers being 0·81 and 1·21.

The following multiplets are established :—

	(s_3) b^3P_0	(s_4) b^3P_1	(s_5) b^3P_2
b^3P-c^3D			
(p_4) c^3D_1	4191·03	4054·50	3947·50
(p_3) c^3D_2		4044·42	?
(p_9) c^3D_3			4200·69
$b^3P-c^3\overline{P}$			
(p_1) $c^3\overline{P}_0$	?	3979·71	
(p_2) $c^3\overline{P}_1$	4181·88	4045·96	3948·98
(p_6) $c^3\overline{P}_2$		4266·29	4158·59

	(p_4) c^3D_1	(p_3) c^3D_2	(p_9) c^3D_3
$c^3D - d^3P$			
$(d_6)\ d^3P_0$	6818·26		
$(d_5)\ d^3P_1$	6754·30	6827·24	
$(d_3)\ d^3P_2$	6684·73	6756·10	6013·68
$c^3D - d^3\overline{D}$			
$(d_2)\ d^3\overline{D}_1$	6499·10	?	
$(s_1'')\ d^3\overline{D}_2$	6155·23	6215·95	5581·83
$(d_1')\ d^3\overline{D}_3$		?	5727·13
$c^3D - d^3F$			
$(s_1'''')\ d^3F_2$	6105·64	6165·11	5540·90
$(d_4)\ d^3F_3$		6722·90	5987·29
$(d_4')\ d^3F_4$			6032·13
	d^3P_0	d^3P_1	d^3P_2
$c^3S - d^3P$			
$(p_{10})\ c^3S_1$	5650·70	5606·73	5558·71

The new designations of Meissner's terms in accordance with Hund's theory are indicated.

II. Arc Spectrum of Krypton.

We have found 49 constant separations, some of which have already been mentioned by Paulson,[3] and two groups of lines.

	λ	Δν	λ	Δν	λ	ΣΔν
A_1	5823·7	460·7	5993·8	648·8	6236·4	1109·5
A_2	6236·4	461·1	6421·1	649·9	6700·8	1111·0
B_1	5827·1	648·7	6056·1	822·8	6373·8	1471·5
B_2	5993·8	648·8	6236·4	822·8	6573·8	1471·6

In this spectrum are other groups of lines in which the order of constant separations is inverted, or the values $\Sigma\Delta\nu$ are obtained in two or more different manners. Examples :—

	λ	$\Delta\nu$	λ	$\Delta\nu$	λ	$\Sigma\Delta\nu$
C_1	4362·7	193·8	4399·9	324·7	4463·7	518·5
C_2	4399·9	324·7	4463·7	192·5	4502·4	517·2
D_1	5827·1	477·1	5993·8	171·6	6056·1	648·7
D_2	5893·8	171·6	6056·1	477·2	6236·4	648·8

III. Arc Spectrum of Xenon.

The constant separations obtained are 195 in number. The groups of lines are :—

	λ	$\Delta\nu$	λ	$\Delta\nu$	λ	$\Sigma\Delta\nu$
A_1	7119·2	...	...	...	6655·8	977·8
A_2	6849·8	...	...	...	6419·8	977·6
A_3	6668·6	...	...	...	6259·8	979·0
A_4	4923·1	...	...	...	4697·0	977·7
A_5	4916·5	...	...	...	4691·0	977·5
A_6	4829·7	919·4	4624·3	58·1	4611·9	977·5
A_7	4734·1	...	...	...	4524·7	977·2
A_8	4109·7	...	...	...	3951·0	977·1
A_9	3823·7	921·6	3693·5	55·8	3685·9	977·4
B_1	4923·1	977·7	4697·0	117·3	4671·2	1095·0
B_2	4734·1	977·2	4524·7	116·4	4501·0	1093·6
B_3	3823·7	977·4	3685·9	117·5	3670·0	1094·9
C_1	4923·1	977·7	4697·0	530·6	4582·7	1508·3
C_2	4829·7	977·5	4611·9	534·1	4501·0	1511·6
D_1	6503·9	809·2	6178·6	1371·9	5695·7	2181·1
D_2	6487·5	808·5	6164·1	1368·6	5688·4	2177·1
D_3	6112·4	810·2	5823·9	1372·5	5392·7	2182·7
E_1	7119·2	977·8	6655·8	2168·8	5816·0	3146·6
E_2	4844·3	981·8	4624·3	2163·0	4203·7	3144·8
E_3	4829·7	977·5	4611·9	2162·7	4193·5	3140·2
F_1	4844·3	764·7	4671·2	3684·0	3985·2	4448·7
F_2	4792·6	758·9	4624·3	3684·0	3951·0	4442·9
G_1	6727·7	...	...	...	4829·7	5839·7
G_2	6472·6	...	...	...	4697·0	5839·0
G_3	5716·0	...	...	...	4285·8	5836·4
G_4	5163·8	...	...	...	3967·6	5836·9
G_5	4923·1	810·7	4734·1	5027·7	3823·7	5838·4
G_6	4697·0	810·2	4524·7	5028·0	3685·9	5838·2
G_7	4671·2	809·3	4501·0	5029·1	3670·0	5838·4
G_8	4285·8	...	...	...	3549·8	5836·3

Some of these groups have already been found by Sommer[4].

The complete list of constant separations and irregular groups is published in number 3, Vol. 4, of the "Contribuciones al Estudio de los Ciencios (serie Matematicofisica)" (La Plata).

IV. The Validity of Bloch and Dejardin's Method.

The arc spectrum of argon described by the authors mentioned is not complete. Many lines classified by Meissner are absent, and others belong to the spark spectra (simple ionized atom principally), according to the results obtained by Bloch and Dejardin. The spectra of the two other gases are very probably similar.

An interesting conclusion can, however, be deduced from the data of Bloch, the series established by Meissner and the early observations of Merrill[5]. The following table summarises probable regions occupied by different series :—

——	$1s_n - mp_i$	$2p_i - \begin{matrix} ms \\ md \\ ms' \end{matrix}$	$1s_n - 2p_i$
Argon	3354–4510	5187–6870	6964→
Krypton (probably) ...	4274–4502	5475–6906	7590→
Xenon (probably) ...	3549–4285	5392–7119	8230→

The values of m are : For mp, 3 to 6 ; for ms, 3 to 6 ; for md, 4 to 8 ; and for ms', 4 and 5.

References.

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[3] E. Paulson, Ann. der Physik., Vol. 45, p. 419 (1914).

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XLII.—AN INTEGRATING PHOTOMETER.

By M. G. Bennett, *M.Sc.*, University of Bristol.

Received June 25, 1928.

Abstract.

The paper is a description of a type of integrating photometer designed to measure the total amount of light arriving at a point on the earth's surface, from the sun and sky, irrespective of the position of the sun or of the distribution of cloud. Some measurements made with it, shewing the variation of direct sunlight and of indirect sunlight (arriving from clouds, &c.) throughout a typical day, are given as an illustration of its use.

Preliminary Remarks.

In the problem of visibility as it concerns the meteorologist an important factor is the amount of light falling on the object viewed and on the atmosphere between it and the observer. Obviously, this quantity will very largely control the visibility of the object and the amount of haze in the atmosphere. Further, it will vary between wide limits with the type of weather, amount of cloud, and the time of day, etc. In examining meteorological records, the author has been struck by the lack of data on this question, and the instrument described in this paper was designed to provide a simple method of obtaining them.

What is required is a photometer which will measure the total amount of light coming from the sky to a point on the earth's surface, irrespective of the position of the sun or of the distribution of cloud. Further, the instrument should be robust, simple to manipulate, and cheap, as routine measurements are to be made with it at more than one observatory.

Description of Photometer.

Figs. 1A and 1B represent front and side elevations of a section through the photometer. The novel feature of the instrument is the light integrating part of it, which consists of two opal glass bulbs A and B. The inner bulb B is mounted on an opal glass tube fitted into a cork in the mouth of the outer bulb A. Through this tube a patch of the interior of the inner bulb (shown by a short dotted line) can be viewed. Consider a beam of light incident on the outer bulb A at an angle θ with the horizontal. A certain amount of this will be diffusely transmitted into the interior of A. The illumination at any point in the interior, for a certain size and material of bulb, will be a function of the position of the point and of the angle θ. Similarly a certain proportion of this light will be diffusely transmitted into the interior of the inner bulb B. The brightness of the patch in the interior of B with which we are concerned, will depend upon the position of B and on the distribution of light inside A (that is, on the angle θ). Thus it is fairly obvious that if B were near the top of A the patch in question would be brighter for $\theta=90°$ than $\theta=0°$ or $180°$, assuming the beam to be of constant intensity; if B were now brought near the bottom of A, the brightness for $\theta=90°$ compared with the value for $\theta=0°$ or $180°$ would be reduced. No attempt at a mathematical analysis has been made, but it has been

found experimentally that for bulbs of given size and material, it is possible to find a position of B such that the brightness of the patch in question is independent of the angle θ. This is shown in Fig. 2 in which the brightness produced by a beam of constant intensity incident at varying angles θ is plotted as a polar function of θ. If A receives light from all quarters of the hemisphere of sky the brightness of this patch will be proportional, therefore, to the total intensity of the incident light irrespective of its distribution.

This brightness is measured by comparison with the light from the lamp L.

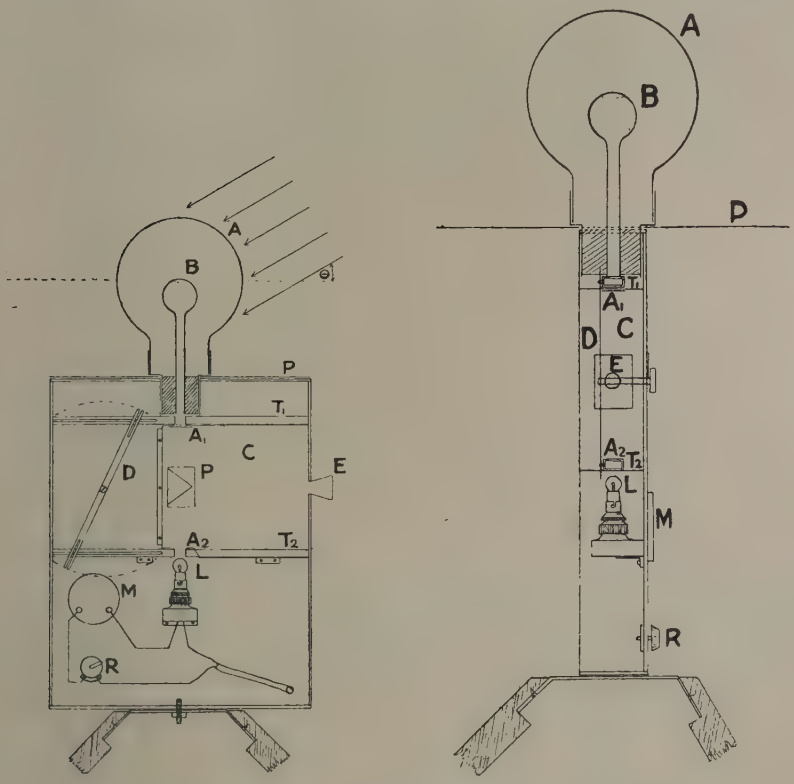


FIG. 1A. FIG. 1B.

DIAGRAMS OF THE PHOTOMETER.

The two illuminations enter the chamber C through the apertures A_1 and A_2, and fall on the two sides of the plaster of paris prism P which is viewed through the eyepiece E. The two sides are matched by means of optical wedge filters which slide in lengths of rectangular tubing T_1 and T_2 over the apertures A_1 and A_2. Their positions are controlled by the rotating arm D which engages in pins cemented to the wedges projecting through slots in the tubing. The axis of D carries a pointer

which moves over a scale on the outside of the instrument. The lamp L is controlled by means of the rheostat R (which has an external handle) and ammeter M. A flexible lead is brought outside to an accumulator. Space is allowed inside for dry batteries, however, if it is desired to make the instrument more portable. The chamber C is lined with black velvet to avoid internal reflections, and over the aperture A_1 is cemented a piece of Flavazine T No. 16 Wratten filter which brings the illuminations to be matched to the same colour. A sheet of iron P painted dead black is placed at the base of the bulbs to minimize the effect of upward reflections from the earth and surroundings.

The instrument has, of course, to be calibrated. This is done by setting up the instrument and the plate of a Macbeth Illuminometer side by side at various distances from a 1,000 c.p. pointolite lamp, and comparing the readings obtained. The range may be altered by using either one of the optical wedges alone or both. With the upper wedge only in use big intensities may be measured and with the lower one small intensities. With both in use the complete double range is included, but there is a corresponding crowding of the scale and loss in accuracy. Typical

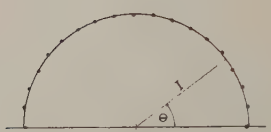


FIG. 2.—POLAR SENSITIVITY OF PHOTOMETER.

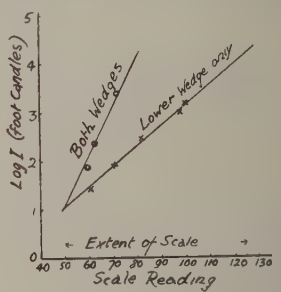


FIG. 3.—CALIBRATION OF PHOTOMETER.

calibration curves are shown in Fig. 3. (In the case of the photometer to which these curves apply, the range when the upper wedge was used alone was far beyond what is likely to occur in this work. It is, therefore, not included in this graph.) Further, the range may be altered to any degree, more or less permanently, by the insertion of neutral filters at either A_1 or A_2.*

To use the instrument, all that has to be done is to adjust the current through the lamp to the standard amount used in the calibration, and then rotate the arm D until a match is obtained. The scale reading of the position of D then gives the total illumination falling on A.

As an example of the use to which this photometer has been put, the following measurements are given of the variation of illumination on the earth's surface throughout a particular day. Fig. 4 shows the observations taken on the tower of the H. H. Wills Physics Laboratory, University of Bristol, on 20th June, 1928. The

* The photometer in reality measures the total flux falling on the sphere A. For the present purpose it was more convenient to express the results in terms of foot-candles, the unit in which the illumination of a perfectly diffusing plate placed horizontally at A would be measured. This can readily be converted into lumens by multiplying by πr^2, where r is the radius of the sphere A.

amount of cloud and opacity of the atmosphere was continually changing throughout the day. On the occasions marked *A* to *F*, the sun was shining brightly. The upper dotted line around these points may be taken as roughly representing the light which would have arrived if the sun had been shining all day. On the occasions *U* to *Z* the sun was obscured by cloud. The lower dotted line represents the amount of light arriving at the observation point indirectly from the sun via the clouds and haze in the atmosphere. The difference between these two lines represents, therefore, the value of the direct sunlight throughout the day. Such results will obviously depend very much on the type of weather.

While the instrument in its present form is sufficiently accurate for the purpose for which it is designed, some improvement is necessary if it is to be used for the measurement of small changes in intensity. It may be pointed out that the opal

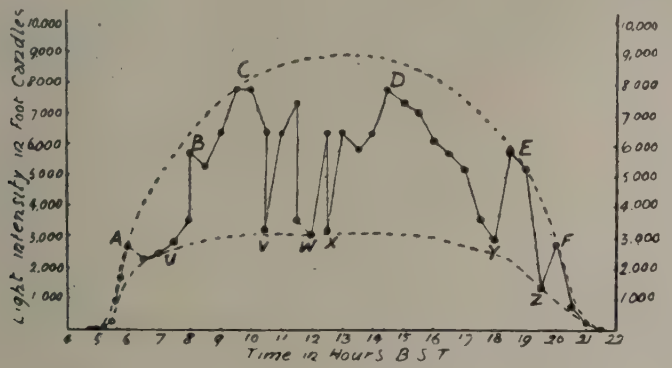


FIG. 4.—VARIATION OF DAYLIGHT AT BRISTOL, JUNE 20, 1928.

glass integrator, in itself, is of sufficient accuracy to be applied to much more delicate work. That this is the case is shewn in the following way. The distribution curve in Fig. 2 was not actually obtained with the prism-wedge system used in the present form of the instrument, but with a photometer of much higher sensitivity, namely, a Macbeth illuminometer. The smoothness of the curve is highly satisfactory. The limitations of the present instrument are, therefore, largely determined by the photometric part of the apparatus. Considerable increase in sensitivity is here possible, such, for instance, as may be obtained by the use of wedges of smaller density gradient.

This work has been carried out in the H. H. Wills Physical Laboratory of the University of Bristol, and I wish to thank Prof. A. M. Tyndall for his kind interest in the work.

XLIII.- SOME RECENT DEVELOPMENTS OF STATISTICAL MECHANICS.

Lecture by J. E. Lennard-Jones, The University, Bristol.

Received June 29, 1928.

Abstract.

Some fundamental changes have been introduced into statistical theory since the publication of a paper by Bose in 1924. The characteristic features of the new statistics, including that of Bose and Einstein, and the later one of Fermi and Dirac, are pointed out in this lecture and compared with the classical statistics. A number of recent applications of the new ideas are described, including the work of Thomas and Fermi on the distribution of electrons in atoms, and the work of Sommerfeld and others on the electron theory of metals. An account is also given of some recent results obtained by the author and H. J. Woods on the distribution of electrons in a metal.

§1. Introduction.

AN unexpected turn has recently been given to statistical theory which adds considerably to its interest, and makes important additions to its scope; so much so that it is now possible, as Thomas[1] and Fermi[2] have shown, to derive certain average properties of the atom by statistical methods. The new departure dates from the publication by Bose[3] in 1924 of a new method of determining Planck's radiation formula. The importance of this work depends not so much on the results attained as on the initial assumptions found to be necessary. Bose modified one of the basic steps in statistical theory—viz., that which is concerned with *a priori* probability. In order that his innovation and others which have been stimulated by his work may be the more fully appreciated, we shall first review some of the main features of classical statistical theory.

The main problem of statistical theory is to determine what are the most probable or the normal properties of an assembly, or, as Fowler[4] would express it, what are the *average* properties of an assembly. The scope of statistical theory is thus limited to the equilibrium properties of an assembly, and is not concerned with such properties as viscosity, diffusion, which only become evident when conditions are non-uniform. The first necessary step is to decide what events are equally likely, or (to put it somewhat crudely) what is the unit of probability.

§2. Liouville's Theorem.

The argument is simplified by reference to generalised space. Suppose that $2s$ co-ordinates are necessary to describe uniquely the position and momenta of each particle (or system), and that the assembly consists of N such systems. (In most of the applications in this Paper we shall consider point systems defined by 3 positional co-ordinates and 3 velocity co-ordinates, so that $s=3$.) A point in a $2Ns$ generalised space then provides a full description of the instantaneous positions and momenta of the whole assembly, and the path of this point gives the life history of the assembly. Not all paths are possible owing to certain conditions imposed on the assembly, such as constancy of total energy. These restricting conditions confine the path to certain surfaces in the $2Ns$ space. It is not, of course, possible

to determine the path of the representative point, for this would involve a complete solution of all the dynamical equations of motions of the whole assembly simultaneously, and would require us to know at any given time the co-ordinates of all the individual molecules of the gas. The problem of statistical theory is to find as much information as possible about the path in the generalised space without actually knowing it in detail. In this connection a theorem due to Liouville is of fundamental importance. Instead of concentrating on the life history of any selected assembly, Liouville considered a large number of identical assemblies started from all conceivable initial conditions, so that the generalised space could be regarded as filled with representative points. He was able to show that, provided the systems obey the ordinary dynamical laws, the density of these points remains constant as they each move along their paths. The result is of considerable importance, as it shows us that there is no tendency for the points to congregate in special regions in the generalised space.

If, therefore, an assembly when left to itself always possesses a certain property P after a sufficient lapse of time, then the above theorem entitles us to assert that the property must be true of the whole of the generalised space.

The argument at this stage is usually supplemented by an assumption, known as Maxwell's assumption of continuity of path, which is tantamount to the assertion that the average properties of any selected assembly taken over a long interval of time is the same as the average taken over a large number of systems. Although this assumption plays a central part in the theory, it has never actually been justified, and this step must be regarded as the least satisfactory in the whole development of statistical theory. However, some such step is necessary if the properties of a single assembly are to be inferred from the behaviour of a large number of assemblies.*

In this way the following answer is reached to the question which we raised above as to what is to be regarded as the unit of probability: *All points in the generalised space are to be regarded as equally likely.*

§ 3. The Classical Statistics.

To illustrate the application of this result to statistical theory we may consider a special problem. We seek the most probable distribution of energy among the N members of an assembly, endowed with translational energy only, given that the total energy is E. For this purpose it is an advantage to consider not only the generalised space mentioned above, but also a phase space of 6 dimensions, x, y, z, p_x, p_y, p_z, the first 3 being the usual positional co-ordinates and the second 3 the co-ordinates of momenta. A single point in this space then describes uniquely the co-ordinates and components of momenta of any *one* member, and N points describe uniquely the whole system; in fact, an array of N points in the phase space gives (so to speak) a "snap-shot" of the assembly, and may be called a *complexion*. For each such array there is one point in the generalised space of $2Ns$ dimensions. (For convenience, we shall now refer to the $2s$ space as the *phase* space, and the more general $2Ns$ space as the *hyper* space.) Now it is clear that many interchanges may be made among the array of N points without altering its distribution as a whole—in other words, many microscopic changes may be made without altering the com-

* For a discussion of this and other difficulties in statistical theories, the reader is referred elsewhere(5) (6).

plexion macroscopically. Every such interchange, however, affects the position of the representative point in the hyper space owing to the re-arrangement of its co-ordinate (just as the point 1, 2, 3 in ordinary space is different from the point 2, 1, 3). The greater the number of possible interchanges the greater the number of points in the hyper space, and the greater the probability that such a complexion will occur. It is in the manner of counting interchanges in a complexion that the theory has been modified, and we must, therefore, explain in detail the method adopted in the classical theory.

The classical method supposes the phase space divided up into a large number of cells, labelled 1, 2, . . . r . . . of equal extension ω. A distribution of N points in the phase space may then be described in terms of the number of points in each cell, say a_1 in cell 1, a_2 in cell 2, and so on. The number of possible interchanges which may be made among the N points without making any perceptible difference to the complexion is

$$W=N\,!/a_1!a_2!\ldots, \qquad (1)$$

for this is the number of ways of allotting a_1 points to cell 1, a_2 to cell 2, out of a total of N points. This is, therefore, the number of representative points in the hyper space of $2Ns$ dimensions. The complexion for which this number is a maximum may be regarded as the most probable, or the normal distribution of the assembly. In order to find the most probable distribution we must find that for which W is a maximum, subject to the conditions that

$$\sum_r a_r=N, \qquad (2)$$

and

$$\sum_r a_r\varepsilon_r=E, \qquad (3)$$

where ε_r is the energy associated with the r^{th} cell. In the simple case we are considering

$$\varepsilon_r=\frac{1}{2}m(\dot{x}_r^2+\dot{y}_r^2+\dot{z}_r^2)=\frac{1}{2m}(p_x^2+p_y^2+p_z^2)$$

(where p_x, p_y, p_z are the components of momentum).

Using a theorem due to Stirling that

$$\underset{a\to\infty}{Lt}\ a\,!=(2a\pi)^{\frac{1}{2}}(a/e)^a, \qquad (4)$$

we then easily find that

$$\frac{\delta W}{W}=-\sum_r\{1+\log a_r\}\delta a_r, \qquad (5)$$

For a maximum, therefore, we have

$$\sum_r\{1+\log a_r\}\delta a_r=0, \qquad (6)$$

together with

$$\sum_r\delta a_r=0, \qquad (7)$$

and

$$\sum_r\varepsilon_r\delta a_r=0, \qquad (8)$$

from (2) and (3) above. These equations are simultaneously satisfied if we write

$$\sum_r\{1+\log a_r+\lambda+\mu\varepsilon_r\}\delta a_r=0, \qquad (9)$$

where λ and μ are Lagrangian undetermined multipliers. If this equation is true for all variations of δa_r, we must have

$$1+\log a_r+\lambda+\mu\varepsilon_r=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

whence

$$a_r=e^{-1-\lambda-\mu\epsilon_r}=Ae^{-\mu\epsilon_r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where A has been written for $e^{-1-\lambda}$ and is as yet an undetermined constant. To determine the constant μ, we use the familiar expression for the entropy

$$S=k\log W, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where, of course, $W_{\max.}$ is now understood. By making a variation in the total energy E and putting $\delta E/\delta S=T$, the temperature, we have

$$\delta S=\frac{\delta E}{T}=k\frac{\delta W}{W}=-k\sum_r\{1+\log a_r\}\,\delta a_r=-k\sum_r\{-\lambda-\mu\varepsilon_r\}\,\delta a_r=k\mu\delta E,$$

so that

$$\mu=1/kT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The constant A is determined from the condition (2),

$$N=A\Sigma e^{-\epsilon_r/kT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the summation being taken over all cells of the phase space. In order to effect this summation it is convenient to group together the terms which have approximately the same energy. To do this, we note that the amount of phase space for which the energy is less than a fixed amount ε is given by an integral of the type

$$I=\int\int\int\int\int\int dxdydzdp_xdp_ydp_z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

taken over the phase space for which

$$\frac{1}{2m}(p_x^2+p_y^2+p_z^2)\leqslant\varepsilon, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The integration with respect to x, y, z is over the whole permissible range of these variables—that is, over the whole volume of the containing vessel—and accordingly results in a factor V. The integral with respect to p_x, p_y, p is over a sphere of radius $(2m\varepsilon)^{\frac{1}{2}}$, and, therefore,

$$I=V\frac{4}{3}\pi(2m\varepsilon)^{3/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Similarly, the amount of phase space for which ε lies between the limits ε_r and $\varepsilon_r+d\varepsilon_r$ is

$$dI=V4\pi(2m\varepsilon_r)d(2m\varepsilon_r)^{1/2}=V(2m)^{3/2}2\pi\varepsilon_r^{1/2}d\varepsilon_r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If we suppose the cells to be of extension ω, we get for the number of cells with energy between ε_r and $\varepsilon_r+d\varepsilon_r$

$$V(2m)^{3/2}2\pi\varepsilon_r^{1/2}d\varepsilon_r/\omega.$$

Grouping now all the terms in the summation (14) of energy between ε_r and $\varepsilon_r+d\varepsilon_r$, we have

$$N=\{A\Sigma V(2m)^{3/2}2\pi\varepsilon_r^{1/2}d\varepsilon_r/\omega\}\,e^{-\epsilon_r/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

On writing A' for A/ω, and replacing the summation by an integral, as we obviously can if the cells have been chosen small enough, we have

$$N=V(2m)^{3/2}2\pi A'\int_0 \varepsilon_r^{1/2}d\varepsilon_r e^{-\epsilon_r/kT}=V(2m)^{3/2}2\pi A'\,.\,\tfrac{1}{2}\sqrt{\pi}\,.\,(kT)^{3/2}. \quad . \quad . \quad (20)$$

so that

$$A'=N(kT)^{-3/2}/V(2m\pi)^{3/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The number of atoms in the gas with energy between ε and $\varepsilon+d\varepsilon$ is then

$$\{2N(kT)^{-3/2}/\sqrt{\pi}\}e^{-\epsilon/kT}\varepsilon^{1/2}d\varepsilon\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

or in terms of velocities

$$4\pi(m/2\pi kT)^{3/2}e^{-(1/2)mc^2/kT}c^2dc,$$

which is the usual Maxwellian Law.

§4. Bose-Einstein Statistics.

The step in this development which has now been modified is in the calculation of W, equation (1). The classical method tacitly assumes that each member of the assembly has an identity which is recognisable in counting possible interchanges. In dealing with light quanta by the statistical methods, Bose[3] saw that the distinction between one quantum and another is lost, and that some other method of counting complexions must be devised. He considered light quanta as particles of energy $\varepsilon(=h\nu)$, with momenta $h\nu/c$ in the direction of its motion, so that

$$p_x^2+p_y^2+p_z^2=(h^2\nu^2)/c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

A 6 dimensional phase space can be constructed as in the previous case to describe the position and momenta of the light particles. The amount of phase space in which ε lies between ε_r and $\varepsilon_r+d\varepsilon_r$ is given by (18), and so the amount of phase space in which ν lies between ν_r and $\nu_r+d\nu_r$ is

$$dI_r=V4\pi h^3\nu_r^2d\nu_r/c^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Bose divided his phase space into cells of extension h^3 (without explaining why*), where h is the usual Planck's constant, so that the number of cells in the above region is

$$V4\pi\nu_r^2d\nu_r/c^3.$$

In dealing with light quanta where the fact of polarisation has to be taken into account, it is necessary to multiply this number by 2, so that we have

$$C_r=8\pi V\nu_r^2d\nu_r/c^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

as the number of cells appropriate to the $d\nu_r$ region.

In counting complexions, Bose concentrates on the cells and not on the particles, and supposes that any selected cell can contain any number of quanta with equal probability. If there are C_r cells in a given region, say the region in which the energy

* As a partial explanation of the choice of h^3 as the extension of the cells, we note (1) that it has the right dimensions, (2) that the ordinary quantum conditions $\oint pdq=nh$ divide up the phase space into cells of extension h^3.

lies between ε_r and $\varepsilon_r+d\varepsilon_r$, the total number of ways of distributing a_r particles among them is

$$(C_r+a_r-1)!/a_r!(C_r-1)!, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

and the total number of ways of arranging the whole assembly is

$$W=\prod_r (C_r+a_r-1)/a_r!(C_r-1)!.$$

In the case of quanta we cannot impose the condition that the number is fixed as with material particles, because light quanta in an assembly can be created and destroyed, though the energy condition is to be imposed as usual—viz.,

$$\sum_r a_r\varepsilon_r=E, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

a_r being the number of quanta of frequency ν_r.

Using Stirling's theorem as before, we have

$$\log W=\sum_r \{(C_r+a_r-1)\log(C_r+a_r-1)-a_r\log r-(C_r-1)\log(C_r-1)\},$$

and making W a maximum subject to (27),

$$0=\sum_r \{\log(C_r+a_r-1)-\log a_r\}\delta a_r, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$0=\sum_r \varepsilon_r\delta a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

so that

$$-\log(C_r+a_r-1)+\log a_r+\mu\varepsilon_r=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

We, therefore, have

$$\frac{C_r+a_r-1}{a_r}=e^{\mu\epsilon_r},$$

that is

$$a_r=\frac{C_r}{e^{\mu\epsilon_r}-1}=\frac{V8\pi\nu_r^2 d\nu_r}{c^3}\cdot\frac{1}{e^{h\nu_r/kT}-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

remembering that a_a and C_r are both large.

The density of radiation of frequency ν is then given by

$$\rho_\nu d\nu=a_r h\nu_r/V,$$

$$\rho_\nu=\frac{8\pi h\nu^3}{c^3}\cdot\frac{1}{e^{h\nu/kT}-1},$$

which is Planck's formula.

The method of counting complexions is, therefore, justified by its success. Einstein[7] thereupon applied exactly the same methods to an ideal monatomic gas, and sought the distribution which made the W of equation (26) a maximum subject to the conditions (27) and the additional one

$$\sum_r a_r=N. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Instead of equation (30) we then get

$$-\log(C_r+a_r-1)+\log a_r+\lambda+\mu\varepsilon_r=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

so that

$$\log\{(C_r+1)/a_r\}=\lambda+\mu\varepsilon_r$$

$$a_r=C_r/\{e^{\lambda+\mu\epsilon_r}-1\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

The constant μ is easily determined as in (13) to be $1/kT$, and λ is determined by summing the equation over all values of a_r. The appropriate value of C_r is obtained from equation (18) on dividing by h^3—that is

$$C_r = V(2m)^{3/2}\, 2\pi\varepsilon_r^{1/2} d\varepsilon_r / h^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

We thus have

$$N = \frac{2\pi(2\pi)^{3/2}V}{h^3} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\lambda + \varepsilon/kT} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The equation (34) for a_r is the equivalent of Maxwell's distribution law in the Bose-Einstein statistics. The two are clearly approximately the same when λ is large, the unit term in the denominator being then negligible. Actually, λ is found to be large for ordinary gases at atmospheric pressure (for example, $e^\lambda = 6 \cdot 10^4$ for hydrogen). The divergence from the classical result only becomes perceptible as the density of the gas increases or its temperature decreases; but obviously any such effect would be masked by the increasing imperfection of the gas under such conditions.

The new distribution law, however, has one or two novel features. Thus the entropy of a gas (deduced from $S = k \log W$) tends to zero as the temperature decreases to zero, while the specific heat increases to a maximum, then diminishes to zero. The vanishing of the specific heat at absolute zero is in accord with Nernst's Heat theorem, but the maximum property has not been observed for any gas, and this fact tends to discredit the statistics, at any rate so far as atoms are concerned. This suspicion has been confirmed by a new line of reasoning, to which we refer in the next paragraph.

§5. The Fermi-Dirac Statistics.

In the theory of atoms a principle known as Pauli's Exclusion Principle has been found to be of wide validity. According to this, a unique description can be applied to any electron in an atom (or in a molecule, for that matter) in terms of quantum numbers. No two electrons have the same set of quantum numbers. The analogy of this in statistical theory is that no two electrons occupy the same cell of phase space. Instead, therefore, of supposing, as Bose and Einstein do, that the occurrence of any number of particles in a cell is an event of equal probability, Fermi[8] and Dirac [9] have independently come to the conclusion that a cell can contain one or none, and that each alternative is equally likely.

If we suppose, as before, that there are C_r cells in a given region, say that in which the energy lies between ε_r and $\varepsilon_r + d\varepsilon_r$, and a_r is the number of particles in that region, then the total number of ways of arranging them so that there is not more than one in any cell is

$$C_r!/a_r!(C_r - a_r)!,$$

and the total number of ways of arranging the whole N particles of the assembly among all the regions is

$$W = \prod_r C_r!/a_r!(C_r - a_r)!, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

subject to the conditions (27) and (32). In this case

$$\log W = \sum_r \{C_r \log C_r - a_r \log a_r - (C_r - a_r) \log (C_r - a_r)\}, \quad . \quad . \quad . \quad . \quad (38)$$

and the same procedure as before leads to

$$\log (C_r - a_r) - \log a_r + \lambda + \mu\varepsilon_r = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

for a maximum. We therefore find

$$a_r = \frac{C_r}{e^{\lambda+\mu\varepsilon_r}+1} = \frac{2\pi(2m)^{3/2}V}{h^3} \frac{\varepsilon^{1/2}d\varepsilon}{e^{\lambda+\epsilon/kT}+1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

with $\mu = 1/kT$ as before. Instead of equation (36) to determine λ we find

$$N = \frac{2\pi(2m)^{3/2}V}{h^3} \int_0^\infty \frac{\varepsilon^{1/2}d\varepsilon}{e^{\lambda+\epsilon/kT}+1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

It is curious that such a fundamental change in the statistics should result in such a simple change in the distribution law. The unit term in the denominator of (34) now becomes positive instead of negative.

The energy of such a system remains finite even at absolute zero. This is to be expected, since only one member is allowed to come to rest. The others fall into cells of as low an energy as possible in the phase space, and all cells up to a certain limit are filled. It is found, in fact, that at low temperatures

$$E = E_0 + \alpha T^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

where

$$E_0 = \frac{2\pi}{5} \frac{VGh^2}{m} \left(\frac{3N}{4\pi GV}\right)^{5/3}, \quad \alpha = \frac{\pi mGV}{6h^2} (2\pi k)^2 \left(\frac{3N}{4\pi GV}\right)^{1/3}, \quad . \quad . \quad . \quad (43)$$

so that the specific heat is proportional to the absolute temperature and vanishes at the absolute zero in accordance with Nernst's Heat Theorem. As there is a finite energy at absolute zero, so there is a finite pressure, given by

$$p = p_0 + \beta T^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

as could also easily be deduced from the relation

$$pV = 2E/3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

which is true for all statistical theories.

If λ is large and positive, the new distribution law (40) differs little from the Maxwellian. This is the case for all ordinary gases except at very low temperatures or very high pressures. Sommerfeld[10] has shown that the condition for proximity to or large divergence from the Maxwellian Law is

$$\begin{aligned} &\text{(i)} \quad \{(2\pi mkT)^{3/2}/h^3N\}V \gg 1 \quad \text{(approx Maxwellian, } \lambda \text{ large and positive),} \\ &\text{(ii)} \quad \{(2\pi mkT)^{3/2}/h^3N\}V \ll 1 \quad \text{(non-Maxwellian, } \lambda \text{ large and negative),} \end{aligned} \quad (46)$$

The first condition is satisfied for ordinary gases at normal temperatures and pressures. When the second condition is satisfied, λ is large and negative, so that the exponential term in the denominator of equation (39) is small compared with unity. This means that for a large range of ε, $a_r = C_r$ approximately, and every cell is filled. The assembly is then said to be *degenerate.*

An example of degeneracy is provided by the free electrons in a metal even

at normal temperatures. Assuming that there is one free electron for every atom of a metal, so that N/V is of order 10^{22} to 10^{23}, we then find for $T=300°$

$$\{(2\pi mkT)^{3/2}/h^3N\}V=2\cdot10^{-4} \text{ approx.},$$

which certainly satisfies the second of the above conditions. It is the small mass of the electron which differentiates it from ordinary gas atoms and leads to the above result.

Sommerfeld calculates that the electrons have each an average energy at absolute zero of about 3 volts, and that the pressure exerted by the electrons is of the order 10^5 atmospheres.

One important consequence of the statistics as applied to electrons in a metal is that the contribution of the electrons to the specific heat is negligibly small. This disposes of a well-known difficulty in the electron theory of metals, and constitutes one of the most striking successes of the new statistics.

§ 6. Comparison of the Statistical Theories.

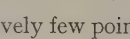
The essential difference between the three statistics considered above may be illustrated by a simple example. Suppose that there were only two members of an assembly, and only two cells in the phase space. The characteristic feature of the classical statistics is that each member is assumed to have an identity, and each is as likely to be in one cell as in another. There are thus four possible arrangements as shown in the figure, and each is

Classical :

to be counted in assigning a weight to the complexion. In the Bose-Einstein statistics, however, the members of the assembly lose their identity, and attention is concentrated on the cell rather than on the individual members of the assembly. In the figure, therefore, the members are represented by indistinguishable points[11].

Bose-Einstein :

Each cell may have any number of points, and so the total number of possible arrangements is three. In the Fermi-Dirac statistics, on the other hand, not more than one representative point is to be in any one cell, with the result that in this simple case only one arrangement is possible. When there are a large number of

Fermi-Dirac : 

cells, and comparatively few points to arrange in them, there is no essential difference between the three methods, because the likelihood of any cell containing more than one point is very small. It is when the number of points is comparable with the number of cells that the three methods lead to divergent results.

Another method of discriminating between the three cases has been given by Brillouin[12]. He makes the fundamental assumption that the presence of a particle in a cell diminishes the *a priori* probability of another particle in the same cell by a fraction β. If, therefore, there are C_r cells in a certain region and a_r particles in the

region, then the number of cells available for an additional particle (the $(a_r+1)^{th}$ particle) is $(C_r-\beta a_r)$. The number of possible arrangements of the a_r particles in the C_r cells subject to this condition is then

$$C_r(C_r-\beta) \ . \ . \ . \ (C_r-\overline{a_r-1}\beta)=\beta^{a_r}\Gamma\left(\frac{C_r}{\beta}+1\right)\Big/\Gamma\left(\frac{C_r}{\beta}-a_r+1\right),$$

where Γ is the usual Gamma function. The total number of possible arrangements for the whole of the phase space is

$$W=N!\prod_r \beta^{a_r}\Gamma\left(\frac{C_r}{\beta}+1\right)\Big/a_r!\,\Gamma\left(\frac{C_r}{\beta}-a_r+1\right),$$

which is to be made a maximum subject to the usual conditions. Brillouin shows that all the statistical theories, classical, Bose-Einstein, and Fermi-Dirac are included in this general method; for the classical case, $\beta=0$, for the Bose-Einstein $\beta=-1$, and for the Fermi-Dirac $\beta=+1$.

The difference between the three formulæ for the number of particles with prescribed energies, equations (22), (34) and (40), lies in a function f, defined in the three cases by

Classical: $$f=e^{-\lambda}e^{-\epsilon/kT}, \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (47)$$

Bose-Einstein: $$f=\{e^{\lambda+\epsilon/kT}-1\}^{-1}, \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (48)$$

Fermi-Dirac: $$f=\{e^{\lambda+\epsilon/kT}+1\}^{-1}, \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (49)$$

This function f is the probability that a cell in the region, where the energy is ε, shall contain a particle. It is to be noted that though the λ's are constants, they are not necessarily the same in the three cases, even when the density and temperature are the same. They tend to become so for small concentrations and high temperatures, and then λ is large and positive. The distribution curves then tend to the usual Maxwellian form. Fig. 1 shows the three distribution curves (f plotted as a function of ε), for an assembly in which the new curves differ appreciably from the classical one; for the Fermi-Dirac case, f is approximately unity for a large range of energies.

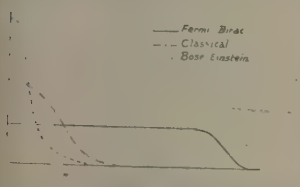


FIG. 1.—THE DISTRIBUTION CURVES IN THE CLASSICAL, BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS.

In the Bose-Einstein statistics λ is essentially positive. Its limiting value is zero, and then f becomes infinite for zero energy. This means that all the representative points in the phase space have crowded into the cell of lowest energy; in other words, the members of the assembly are all at rest. This is the condition of extreme degeneracy. The assembly, therefore, passes from a classical assembly for large values of λ to a state of degeneracy when λ approaches zero. For small values of λ, *particles of low velocity are more frequent than in a classical assembly.*

Degeneracy in the Fermi-Dirac statistics occurs when λ is large and negative, and then f is constant and equal to unity for a large range of ε, after which it decreases exponentially like the Maxwellian law. All the cells of low energy in the phase space are then filled. *Particles of low velocity are less frequent than is indicated by Maxwell's law.*

§7. The Distribution of Electrons in Heavy Atoms.

An interesting application of the ideas outlined above has been made by Thomas[1] and recently also by Fermi[2]. Thomas supposes the electrons in an atom to be degenerate in the sense of Fermi and Dirac. In this case, however, there is a new condition to be imposed—viz., that electrons shall not have sufficient energy to take them out of the field of the atom. This places a restriction on the amount of phase space available. Thus

$$\frac{1}{2m}(p_x^2+p_y^2+p_z^2)\leqslant eV, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

where V is the potential inside the atom. We here assume that relativity considerations can be neglected. For an electron whose positional co-ordinates lie between x, y, z, and $x+dx$, $y+dy$, $z+dz$, the amount of phase space is limited by a sphere in the p_x, p_y, $\ldots$ space of radius $(2meV)^{1/2}$, so that the total amount available is

$$\frac{4}{3}\pi(2meV)^{3/2}dxdydz.$$

The number of cells in this phase space is

$$\frac{4}{3}\pi(2meV)^{3/2}dxdydz/h^3.$$

If the position and momenta of the electrons could be defined by six co-ordinates, this phase space would be sufficient; but it is now found necessary to attribute to each electron a spin, and the axis of spin can point in one or other of two opposite directions. This requires a new co-ordinate to specify the position and motion of an electron, or, alternatively, we can suppose by an extension of the Pauli Exclusion Principle that not more than one electron of prescribed spin can exist in a cell of extension h^3 in the six-dimensional phase space. Two electrons can co-exist in the same cell provided they have opposite spins. The assumption of degeneracy in an atom is equivalent to assigning two electrons to each available cell of the phase, so that the number of electrons permitted within $dxdydz$ is

$$2\left\{\frac{4}{3}\pi(2meV)^{3/2}dxdydz\right\}/h^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

If ρ denotes the electric density, we have

$$\rho=\frac{8}{3}\pi e(2meV)^{3/2}/h^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

Now since the potential V is determined by the nuclear charge and the electron distribution round it, V is determined by Laplace's equation. Hence

$$\Delta^2V=-4\pi\rho=\frac{32}{3}\pi e(2meV)^{3/2}/h^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

which is a differential equation to determine V. The constants of the solution are determined by the conditions that

$$\left.\begin{aligned} Vr&\to E \quad \text{as} \quad r\to 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ V&\to 0 \quad \text{as} \quad r\to\infty, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned}\right\} \quad (54)$$

E being the charge on the nucleus.

Thomas has solved the equation by numerical methods, and has drawn up

tables from which may be inferred the variation of ρ and V with r. The potential is found to be proportional to $E^{4/3}$, so that the distribution of electrons is the same in all atoms (on this theory) except as regards scale. The treatment is only approximate, as it does not indicate the existence of atomic levels, and only gives a "smoothed-out" distribution. Fig. 2 shows the radial density $4\pi r^2\rho$ of Rb^+, obtained by this method as a function of r. The same figure includes the corresponding results for Rb^+ obtained by the more accurate (though more laborious) calculation of Hartree[13]. The unit of length is the radius of the Bohr 1_1 orbit for the hydrogen atom. The ordinate is the radial density $4\pi r^2\rho$, or the rate of change of effective nuclear charge Z.

Fermi[2] has recently considered the same problem independently, and has obtained similar results. He has further applied his results to calculate the angular momentum of the electrons in an atom. The number of electrons in any element $dxdydz$ is known from the above work, and the distribution of their velocities can easily be deduced, since all cells in the phase space determined by equation (50) contain two electrons, so that the fraction of electrons in the element with prescribed angular momentum P to $P+dP$ can easily be deduced. It is thus an easy matter to calculate the total number of electrons in the atom with the same prescribed angular momentum. Taking the usual relation between angular momentum and the azimuthal quantum number k—viz., $P=kh/2\pi$—Fermi is thus able to deduce the total number of electrons in an atom with a prescribed azimuthal quantum number, and thus the number of electrons in the s-, p-, d-, f . . . states, since for these states $k=1/2$, $3/2$, $5/2$, $7/2$ . . . (in the old quantum theory). The result is compared with Stoner's[6] distribution in the various atoms of the periodic table. The theory indicates the atomic number for which the s-, p-, d-, f- electrons first begin to appear—viz., Z (atomic number)$=1$, 5, 21, 55. This is in accordance with accepted results that the p- terms begin at Boron($Z=5$), the d- terms in Scandium ($Z=21$) and the f terms in Cerium ($Z=58$).

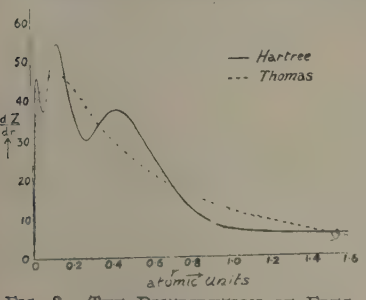


FIG. 2.—THE DISTRIBUTION OF ELECTRONS IN Rb^+.

Milne[14] has used the method and results of Thomas to calculate the total ionisation potential of a heavy atom $\Sigma\chi_r$, where χ_1, χ_2, . . . are the energies required to remove the first, second . . . electrons from the atom. He finds the simple result that

$$\Sigma\chi_r = 17Z^{7/3} \text{ volts} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

for an atom of atomic number Z. Thus for iron ($Z=26$), $\Sigma\chi_r=34{,}000$ volts, and for silver ($Z=47$) $\Sigma\chi_r=136{,}000$ volts, while other more accurate methods[15] give 33,600 and 138,000 volts respectively. Such estimates of the total ionisation potential are useful in astrophysical investigations.

§ 8. THE SUSCEPTIBILITY OF METALS.

It is a well-known fact that many metals (especially the alkalis) exhibit only slight paramagnetic properties and the susceptibility is practically independent of temperature. It has hitherto been impossible to explain these facts either by

supposing the magnetic properties to be due to the atomic cores or to the known magnetic moment of the valency electrons. All attempts to construct a theory on classical lines have led to a variation of susceptibility with temperature. Recently Pauli[16] has attempted to explain the observed facts on the supposition that it is the moment of the valency electrons which play the central rôle, and that the new Fermi-Dirac statistics must be used instead of the classical.

In the presence of an external field, the axis of a magnetic moment can take up only certain quantised directions, defined by a quantum number m, which is a measure of the component of magnetic moment along the field. The number m can take only certain discrete values (either integers or half integers) defined by the limits $-j \leqslant m \leqslant j$, where j is the total magnetic quantum number. In applying these ideas to an electron gas, Pauli assumes as a rational generalisation of the Exclusion Principle that no two electrons can exist in the same cell of the phase space with the same quantum number m. The maximum number of electrons in a cell is thus equal to the number of possible values of m between $\pm j$. When the maximum number is present their net contribution to the magnetic moment is zero.

The energy of an electron is now made up of two parts, an energy of translation ε_r and a magnetic energy φ_m. The distribution of electrons in the region of the phase space for which ε lies between ε_r and $\varepsilon_r + d\varepsilon_r$ is not now given by equation (40), but by a modification of it—viz.,

$$a_{r,m} = \frac{V \cdot 2\pi(2m_0)^{3/2}}{h^3} \frac{\varepsilon_r^{1/2}\, d\varepsilon_r}{e^{\lambda+(\varepsilon_r+\varphi_m)/kT}+1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

We have here used m_0 to denote the mass of the electrons to differentiate it from the magnetic quantum number m.

The constant λ is obtained by summing the equation over all values of a_r (that is, by integrating over all values of ε_r) and equating the result to the total number of electrons N. The total number of electrons with magnetic energy φ_m is then

$$N_m = \frac{V \cdot 2\pi(2m_0)^{3/2}}{h^3} \int_0^\infty \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{\lambda+(\varepsilon_r+\varphi_m)/kT}+1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

and the magnetic moment M of the whole assembly is given by

$$MH = -\sum_{m=-j}^{m=+j} N_m \varphi_m. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

Now the magnetic moment of an electron is equal to $eh/2\pi m_0 c$, and so

$$\varphi_m = -mH(eh/2\pi m_0 c). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Substituting in the expression above, Pauli finds for the susceptibility (for weak fields)

$$\chi = (N/V)^{1/3}(2{\cdot}209)10^{-14} = n^{1/3}(2{\cdot}209)10^{-14}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

n being the number of electrons per unit volume. This expression is independent of temperature as required by experiment, and moreover yields absolute values of

susceptibilities in satisfactory agreement with the observed values. Pauli gives the following results—

	Na	K	Rb	Cs
$X_{calc.}$ $0{\cdot}10^7$	6·57	5·2	4·88	4·54
$X_{obs.}$ $0{\cdot}10^7$	5·8	5·1	0·6	−0·5

It is to be anticipated that the observed values will be less than the calculated, owing to the diamagnetic effect of the core. This will increase with the size of the core, and it is not surprising to find that it is sufficient in the case of Cs to neutralise the paramagnetic effect of the electrons and to render the metal as a whole diamagnetic.

Frenkel[17] in a paper which has just appeared, has given a simpler though less general method of arriving at the above formula for susceptibility. Frenkel's treatment is limited to conditions at the absolute zero.

The obvious defect in Pauli's work is the neglect of the interaction between electrons and atomic cores. The ordinary electrostatic attraction is never mentioned, though it seems fairly clear that this will modify the statistical distribution of electrons in the metal, just as in Thomas's treatment of electrons in an atom. The method is equivalent to considering an assembly of electrons in a closed box and neglecting their interaction except in so far as this is represented by the Pauli Exclusion Principle.

§ 9. The Electron Theory of Metals.

The work of Pauli on the statistics of electrons in metals has stimulated Sommerfeld[10] to consider the whole electron theory of metals in the light of the new statistics. We have already referred to some of Sommerfeld's results. It remains to discuss his investigations of electrical and thermal conductivities and allied phenomena, though it is beyond the scope of this review to enter into the new theories in any detail.

The distribution function f given in equation (49) is symmetrical in the momentum co-ordinates, which enter only through ε, so that particles with a prescribed energy are equally distributed in directions. When, however, conditions are unsymmetrical, as they are when an electrical field is applied in a given direction, or when there is a temperature gradient, the function f no longer gives the correct distribution law. If, for simplicity, we suppose the non-uniformity of conditions to be confined to one direction (say along the x-axis), f becomes changed from its initial value f_0 (say) to

$$f=f_0+\xi\chi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

where χ is a function of ε only, and ξ is the component of velocity in the x-direction. Lorentz[18] has shown how to obtain f when f_0 is known, though he, of course, assumed the Maxwellian distribution for f_0. He showed, in fact, that when an electric field F is applied in the x-direction

$$f-f_0=-\frac{l}{v}\left(\frac{eF}{m}\frac{\delta f_0}{\delta\xi}+\xi\frac{\delta f_0}{\delta x}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

where l is the free path of the electrons (assumed to be a function of velocity). When f is once obtained, it is easy to deduce the net flow of electrons across a given plane

under the influence of the external field, and similarly the net flow of energy owing to a temperature gradient.

Using the f_0 determined by the Fermi-Dirac statistics, equation (49), Sommerfeld is led to the following formulæ :—

——	Electrical conductivity (σ)	Thermal Conductivity (κ)	Ratio (κ/σ)
New theory	$\frac{8\pi}{3}\frac{e^2 l}{h}\left(\frac{3n}{8\pi}\right)^{2/3}$	$\frac{8}{3}\pi^3\frac{lk^2T}{h}\left(\frac{3n}{4\pi}\right)^{2/3}$	$3{\cdot}3\left(\frac{k}{e}\right)^2 T$
Classical theory ...	$\frac{4}{3}\frac{e^2 ln}{(2\pi mkT)^{1/2}}$	$\frac{8}{3}\frac{lnk^{3/2}T^{1/2}}{(2\pi m)^{1/2}}$	$2\left(\frac{k}{e}\right)^2 T$
Experiment	$\propto 1/T$	independent of T	$(3\,..\,3{\cdot}5)(k/e)^2 T$

Except in so far as the free path l depends on the temperature (though the relation is left undetermined), Sommerfeld's formula for the electrical conductivity is independent of temperature, whereas actually the electrical conductivity of metals is inversely proportional to the temperature. The formula for thermal conductivity similarly fails to account for the observed facts by a factor T, but the Wiedemann-Franz law, as in most theories, is preserved. Moreover, the numerical factor in the ratio of κ/σ is closer to the observed value than that of any previous theoretical formula.

An attempt has been made by Houston[19] to improve Sommerfeld's theory by treating the electrons as waves in accordance with the ideas of de Broglie[20]. As the mean velocity of the electrons according to the new statistics is of the order of a thousand kilometers a second, the equivalent wave-length is about 5 Å., and corresponds to white X-rays. Instead of considering encounters between electrons and atoms in the usual way, Houston calculates the scattering of the electron waves by atomic centres, and takes into account the heat motion of the atoms in the same way that Debye[21] has done for X-rays. He finds that the electrical conductivity varies inversely as the temperature for normal temperatures and inversely as the square of the temperature at very low temperatures. The theory is, therefore, in accord with facts at high temperatures, and indicates a rapid increase in the conductivity at low temperatures, as is also required by observation. The theoretical increase at low temperatures is, however, not as great as that found experimentally. Nevertheless, the theory is more successful than any other in its interpretation of the dependence of electrical conductivity on temperature ; but, like all other theories, it fails to account for the phenomenon of superconductivity. This still remains a mystery.

An observed property of metals which would at first sight appear to be at variance with the new statistics is the velocity distribution of electrons emitted at high temperatures. This has been shown by Richardson[22] and others to be of the Maxwellian type, whereas the velocity distribution inside the metal, according to the new statistics, is completely different from this. (*See* Fig. 1.) The new theory, however, yields a formula for electron emission as satisfactory, if not more satisfactory, than the old theory. The two formulæ for the number of electrons emitted by a metal are

$$J \propto T^{1/2} e^{-W/kT} \quad \text{(Classical)}, \quad (63)$$

$$J \propto T^2 e^{-(Wa-Wi)/kT} \quad \text{(Sommerfeld)}, \quad (64)$$

where W is the energy of the electrons emitted. In the Sommerfeld formula a new term W_i appears. This represents the effect of the high energy of the electrons inside the metal, for, as was pointed out in a preceding paragraph, the average energy at absolute zero is of the order of 2 to 3 volts.

The appearance of the exponential in the Sommerfeld formula is due to the fact that the new velocity distribution curve, while approximately constant for a large range of energies, does eventually fall off exponentially, and it is only the high energy electrons which emerge from the metal. The new statistics is, therefore, successful in producing a satisfactory formula for electron emission; in fact, a formula of the type (64) had previously been suggested by Dushman[23] from other considerations, and had been shown to be in better agreement with the observations than (63).

Other phenomena dealt with by Sommerfeld include the Volta effect, Hall effect and various allied thermomagnetic phenomena; but we cannot enter into an account of these investigations here. For these the reader is referred to the original papers[24], [25].

§10. The Distribution of Electrons in a Metal.

A defect in Sommerfeld's work is the neglect of the interaction of electrons and atomic cores in calculating the statistical distribution. No theory of metals can be regarded as adequate which does not include the assembly of electrons and atomic cores in one system to be treated as a whole. Recently the author, in collaboration with H. J. Woods,* has attempted to find the average distribution of electrons in a metal in the same way that Thomas[1] and Fermi[2] have done for isolated atoms. The mathematics for a three-dimensional array of atoms, however, proves intractable, and the problem has, therefore, been simplified by considering atoms as long and chain-like (like hydrocarbons, for instance) packed in a two-dimensional square array. The nuclei can then be regarded as line charges arranged in a square lattice, surrounded by enough electrons to make the system as a whole electrically neutral. We consider a section of this array bounded by two parallel planes at right angles to the nucleus and distant a apart.

In order to apply the condition of degeneracy, we suppose that the velocity of all the electrons parallel to the nuclei is the same, and is determined by a de Broglie wave of wave-length $2d$. The momentum in this direction is then given by

$$p_z = \pm h/2d. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

In the other directions, p_x and p_y are limited by the condition that the kinetic energy plus potential energy shall not be positive. The assumption that the system is degenerate, and therefore has 2 electrons in every cell of extension h^3 of the phase space, leads to a differential equation analogous to equation (53), obtained by Thomas and Fermi—viz.,

$$\frac{\delta^2 V}{\delta x^2} + \frac{\delta^2 V}{\delta y^2} = k^2 V, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

where

$$k^2 = 16\pi^2 mc^2/dh^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

This equation has to be solved subject to the conditions that $V \sim \log r$ near each

* To be published shortly.

nucleus, and that V is doubly periodic in the x, y plane. The solution of this equation leads to a pattern of equipotential lines (which are also lines of equal density) shown in Fig. 3. The nuclei are indicated by crosses.

Near a nucleus the equipotential lines are approximately circles. These are gradually deformed until a curve is reached shown by the continuous line which extends through the crystal. An electron on this line can travel about the crystal without doing any work. The equipotential lines enclose another system of closed curves which surround the centres of the squares. The electrons in these regions may be regarded as shared electrons, while the others are more definitely bound to a nucleus. The shared electrons form a lattice array which interpenetrates that of the nuclei. This provides some justification for the model of a metal, proposed by J. J. Thomson[26] and Lindemann[27], in which the valency electrons form a rigid lattice interpenetrating that of the atomic cores.

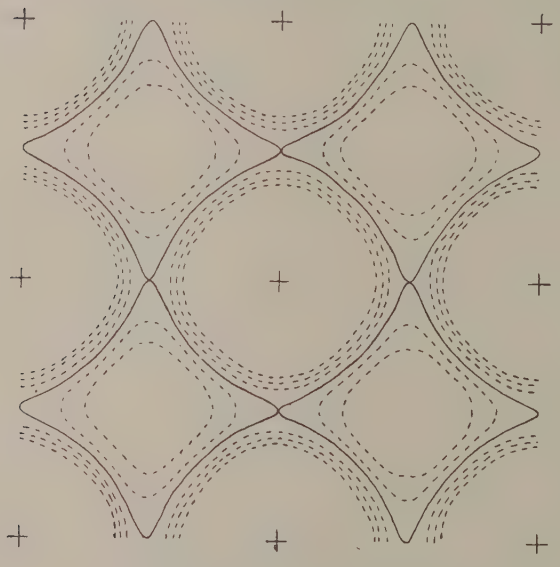


FIG. 3.—THE DISTRIBUTION OF ELECTRONS IN A METAL.

§11. THE STATISTICS OF GASEOUS MIXTURES.

An important extension of statistical theory has been made by Jordan[28] to assemblies of different particles (or systems), including cases when one set of particles obey one statistics and another set a different statistics. He has applied his results to a number of interesting astrophysical problems, including that of the equilibrium of a system of protons and electrons. In the latter he assumed with J. J. Thomson that electrons and protons can annihilate one another and set free a quantum of radiation. Bothe,[29] too, has considered mixed assemblies, and has obtained a general formula for the equilibrium constant in a chemical reaction.

Fowler[30] has dealt with these and similar problems in a comprehensive manner. In recent years Fowler has made enormous improvements in the mathematical technique of statistical theory. Instead of calculating the most probable states of an assembly, Fowler calculates average properties by summing over all parts of the generalised phase space, and in this connection is able to introduce a powerful theorem in complex integration. The ultimate results are, of course, the same as those obtained in the usual way, but there is considerable gain in elegance and in mathematical rigour. The method is capable of dealing with the new developments outlined above as well as with the theory of electrolytes, assemblies of ions and

electrons as in giant stars, and other extensive applications. It would, however, take us too far even to review the achievements of the theory in such varied fields of inquiry.

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DEMONSTRATION ON SOME RECENT STUDIES IN ALTERNATING MAGNETISM AND SOME POSSIBLE APPLICATIONS.

By W. M. Mordey, *M.I.E.E.*, *M.Inst.C.E.*, at the Bessemer Laboratory, Royal School of Mines.

THIS demonstration followed the lines of a Discourse given by the lecturer some years ago before the Royal Institution,* with some references to later developments.

In most of the experiments pulverised materials were used to enable Faraday's simple lines-of-force method of study to be used, and because of possible applications to the concentration of crushed minerals. Ordinary lines of force over a permanent magnet were shown with iron, nickel, cobalt, magnetite and pyrrhotite. Specular hæmatite when free from magnetite was unaffected. On trying the same materials over one pole of a small 1-phase a.c. bar magnet the lines of force of iron, nickel, cobalt and magnetite were the same as over the permanent magnet, but pyrrhotite differed; near the pole it formed ordinary radial lines of force, but when the cardboard on which the particles were sprinkled was lifted an inch or more above the pole there was a double effect—a halo caused by hysteretic repulsion was formed at a distance of several inches from it, the radial formation being weakened. On lowering the cardboard—i.e., increasing the field—the halo disappeared, the particles rejoining the radial lines of force, i.e., repulsion was changed to attraction.

With specular hæmatite a halo was formed in either a weak or a strong field, being larger with the latter. No radial lines of force were formed. Repulsion always prevailed over attraction.

With 1-phase multipolar magnets the coalescence of the halos round the poles formed distinct "equatorial" lines, which by Faraday's definition would denote diamagnetism; but he worked with direct current, and his definitions had reference to that only, and do not apply in the present case. The halos show no sign of mutual polar action between the particles.

In the field of 1-phase magnets there were thus three classes of effect :—

(i) With the more strongly magnetic substances of lines of force of the ordinary or direct current type were formed representing attraction.

(ii) With the moderately magnetic substance pyrrhotite both attraction and repulsion took place, the former represented by ordinary lines of force, and the latter by a halo, which increased as the field was weakened, or the cardboard raised.

(iii) With specular hæmatite, the least magnetic of the substances used, a halo formed was round the pole representing repulsion and there were no ordinary lines of force.

In multiphase fields with multipolar magnets several new phenomena were observed—e.g., even with good magnetic iron hysteretic repulsion from the poles took place with weak fields, while with strong fields attraction predominated, and the material was drawn towards the poles and propelled along over the poles in a direction depending on the phase relation.

* Proc. Royal Instn., Vol. 24, Part 1, pp. 267-288 (1923).

The change from attraction to repulsion as the field was weakened was shown by placing the material on a thin board resting at one end on the magnet, and sloping upward so as to make the air gap gradually increase to several inches. The material was propelled up this incline by the multiphase action, spreading out laterally as it ascended and leaving bare the region over the poles. In strong fields what were called " planes of force " were formed by the building up of the material into fins by vertical repulsion from the poles, fed by the propulsion of material along the line of poles, the fins being separated longitudinally by lateral repulsion due to their magnetically equipotential condition.

But with specular hæmatite hysteretic repulsion always predominated over attraction, owing to the fact that its hysteresis coefficient was several hundred times greater than that of good iron, and its permeability probably not much over unity.

Practical mineral concentration was demonstrated by passing powdered ore down wooden shutes placed over long narrow multiphase magnets, the material as it descended separating into two streams, one the amenable constituent, and the other the inert gangue.

That these hysteretic materials were capable of exerting a considerable torque in multiphase fields was shown by the rapid spinning of a rough piece of pyrrhotite rock over the poles of a multiphase magnet, and by little model motors having rotors of various hysteretic substances without winding mounted on a spindle and placed in the field of a multiphase magnet.

There were no eddies, as the materials were either of very high specific resistance or were made practically non-conducting by fine division, and in some cases by mixing with an insulating cement.

In his Royal Institution paper the lecturer gave his reasons for attributing the repulsion to hysteresis. He sees no reason for changing that view.

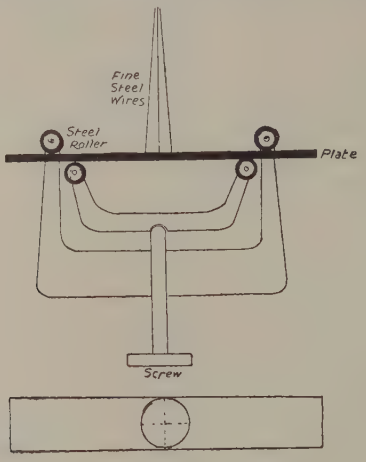
In that paper fuller explanations of some of the effects, for which there is not space here, are attempted.

DEMONSTRATION OF VARIOUS METHODS OF MEASURING POISSON'S RATIO.

By J. P. Andrews, *M.Sc.*

FOR this demonstration a number of pieces of apparatus designed to measure Poisson's Ratio by the method of bending were exhibited and explained. They consisted of copies, as close as possible, of actual experimental arrangements previously used in research, and included:

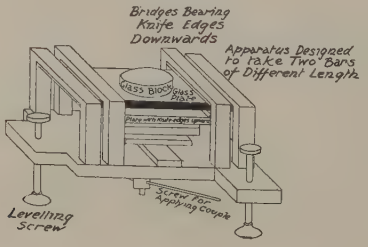
1. *A. Mallock's Apparatus*,* in which the two anticlastic curvatures are



Mallock's Apparatus.

measured by the motion of the ends of four spines erected around the centre of the horizontal surface of a bar bent by couples at its ends.

2. *R. Straubel's Apparatus*,† an elaboration of Cornu's original interference


Bridges Bearing Knife Edges Downwards
Apparatus Designed to take Two Bars of Different Length
Glass Blocks
Glass Plate
Screw for Applying Couple
Levelling Screw

R. Straubel's Apparatus.

method (1869), which was itself an extension of Newton's Rings to anticlastic instead of spherical surfaces. In Straubel's apparatus a complicated arrangement of knife edges is introduced to secure an even pressure on the glass bar.

* Phil. Mag. (1879).

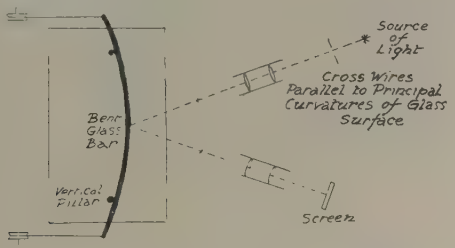
† Ann. d. Physik, 68, p. 369 (1899).

3. *I. Williams' Method,** in which the transverse curvature is measured by the rotation of a mirror suspended by a Kelvin bifilar, which itself depends from the tops of two rods fixed respectively to the two sides of the bar used.

4. *H. Carrington's Method.*†—The spines of Mallock's experiment are replaced by mirrors upon small pillars; and in order to eliminate any correction due to the translatory motion of these mirrors, the pillars are of a definite, calculated length, and the mirrors inclined at a definite angle to the vertical.

5. *H. T. Jessop's Method.*‡—An improvement of the Cornu method in so far as the glass bar under test may be bent in both directions to eliminate the effect of initial curvature.

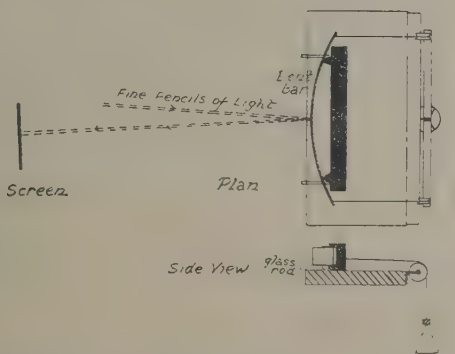
6. *G. F. C. Searle's Method.*§—The distance between the focal lines in the



G. F. C. Searle's Focal Line Method.

image of an object seen by reflection in an anticlastic surface is employed here to determine Poisson's Ratio for glass.

7. *The Method of A. Ferguson and J. P. Andrews* (1928).—Four fine pencils of light are reflected directly from the polished surface of a bent brass



Apparatus of A. Ferguson and J. P. Andrews.

plate to replace the spines of Mallock's experiment. The deflection of the reflected pencils, as observed by reception on a distant screen, enable Poisson's Ratio to be determined.

* Phil. Mag., 24, p. 886 (1912).
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DEMONSTRATION OF A SIMPLE PRACTICAL APPLICATION OF THE PROPERTIES OF SELENIUM CELLS.

By Geo. P. Barnard, The National Physical Laboratory.

THE experiment shown was a development of a demonstration given before the Society in 1926* by Prof. Hans Thirring. The light from a 1000 watt gas-filled lamp was interrupted by a large perforated metal disc (2 ft. in diameter) driven by a small d.c. motor. Circular holes, $\frac{3}{4}''$ in diameter, were drilled in the disc as follows:—Five concentric circles of radii $3\frac{3}{8}''$, $5\frac{1}{8}''$, $6\frac{7}{8}''$, $8\frac{5}{8}''$, $10\frac{3}{8}''$ respectively were ruled on the disc. At equidistant distances along the circumferences of the five circles, 15, 16, 18, 20, 21 holes respectively were drilled. The ratios of the numbers of these holes correspond to the frequency ratios of the following notes in the natural diatonic scale—viz., E, F, G, A, B♭. A wooden shutter was set up close behind the metal disc, so that a selenium cell could be conveniently moved on to any of the five circles of holes.

A Fournier d'Albe type selenium cell having a light-sensitive area of approximately $\frac{3}{4}'' \times \frac{3}{4}''$ was connected in series with a 50 volt battery to the primary of an inter-valve transformer, the secondary of which was connected to the input circuit of the detector valve of a 2-stage resistance-capacity coupled amplifier. A large loud-speaker was placed in the plate circuit of the last valve.

The selenium cell could thus be exposed in turn to intermittent illumination of five different acoustical frequencies, and the fluctuations in current through the cell, amplified as described, produced the corresponding notes in the loud-speaker.

By this means the first part of the National Anthem was played, and was clearly audible throughout the theatre. By the simple expedient of altering the speed of the motor driving the disc the fundamental tone could be changed.

The demonstrator pointed out the extraordinary quickness of response of the electrical resistance of selenium to intermittent illumination of acoustical frequency, and suggested that applications of selenium cells based on this would prove very efficient.

* Proceedings, Vol. 39, p. 97.

ELECTRICAL METHODS OF HYGROMETRY.

AUTHORS' reply to discussion on Paper by Messrs. P. W. BURBIDGE and N. S. ALEXANDER (*see* page 153).

In reply to Professor Tyndall: The more rapid rise of the saturation curve in dry air (Fig. 6, curve IV) appears to be due directly to the greater mobility of ions in dry air. In reply to Dr. Griffiths: No experiments were performed to ascertain if the cotton exhibited any gradual change in its electrical properties at a definite humidity, over a long period of time.

We regret that at the time of publishing, we were not aware of the work done by Mr. F. P. Slater. We find, however, that in general the lag in the change of electrical conductivity with humidity may to a great extent be attributed to the time required for the air to reach equilibrium with the solution. This effect was not entirely eliminated even by rapid circulation of air by means of a fan. It was eliminated, using the apparatus of Fig. 3, by arranging for the change in humidity to be brought about merely by the mixing of the air in the large box with that in the hygrometer box, the solution having been removed. Lag was still found, however, and this we have attributed to the cotton itself. It is to be remembered that experimental conditions are of great importance; for example, the walls of the containing vessel exercise a marked effect. Using the apparatus in Fig. 3, we found initially very large lag effects due to the wooden walls, which gave off water vapour or absorbed it from the air when a change in humidity was made. This was eliminated by covering the wood with paraffin wax. The apparatus used by Slater would apparently permit considerable lag in the rate of acquisition of equilibrium between the air and the solution.

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